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A SHORT COURSE
IN
INORGANIC QUALITATIVE ANALYSIS.

FOR ENGINEERING STUDENTS.

BY

J. S. C. WELLS, PH.D.,
Instructor in Analytical Chemistry, Columbia University.

7

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PREFACE.

THE object of this book is to give a short but thorough course in inorganic qualitative analysis for the use of students who have only a limited time to devote to the subject.

Experience has shown that Fresenius' manual, while invaluable as a work of reference, is too complicated and voluminous for the beginner, the great mass of information there given confusing him, and he becomes discouraged at his inability to assimilate it.

In preparing the present work the idea has been, while still following the general plan of Fresenius, to give only that which seemed essential to a clear understanding of the subject and to make it as concise as possible. For this reason only the more important reactions of the different metals and acids have been given, and the separations are presented in the form of schemes accom-

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panied by explanatory notes, and tables of scheme reactions. The latter have been found of much benefit in helping the student to understand the various reactions taking place in an analysis, as they show at a glance the effect produced by each reagent used.

In the notes the aim has been to call attention to likely sources of error, and to give any explanations as to conditions, etc., that seemed necessary.

The separations used differ in some cases from those of Fresenius, particularly the separation of the first four groups in presence of phosphates, and that of the third and fourth with potassium hydrate when chromium is present; also the scheme for the detection of the acids. All of these methods have been thoroughly tested in the laboratory by large numbers of students, and found to be very reliable and less complicated than those in general use.

Chemical equations are freely used to explain the various reactions taking place in the individual tests as well as in the separations. In the introduction a short explanation is given of these equations and how to write them; also the definitions of certain terms. This, of course, belongs more properly to general chemistry, but experience has proved the average student to be woefully ignorant in this respect, and a brief exposition of the subject seemed necessary.

No attempt has been made to give full description of apparatus, it being considered better for the teacher to do that in the class-room, and he can at the same time perform any of the more difficult tests that may seem to require such demonstration.

There are some who consider it simply a waste of time to begin with the individual reactions of each metal before taking up the separations, but it certainly seems more logical to first study the reactions of the different elements group by group, and then proceed to separate them, rather than to reverse this order and begin with the separations. By restricting the tests to be performed to those actually used in the analysis the number made will not be very large. If time permits these may be increased later on by making use of other methods of analysis, thus bringing in new reactions, but this should not be attempted until the student is thoroughly familiar with at least one good method of separation for all the bases and acids. The work can be made more interesting by giving out for analysis as many natural or commercial products as possible, such as ores, alloys, etc. This can be done almost from the first by beginning with such minerals as calcite, dolomite, etc., and as the work progresses those containing a greater number of bases can be given; care being taken, however, to give only those compounds that are easily soluble in acids, and whose acid radicals do not interfere with the analysis. By thus making practical application of his knowledge the interest of the student is excited, and his work becomes a pleasure rather than a task.

J. S. C. WELLS.

COLUMBIA UNIVERSITY, April, 1898.

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ABBREVIATIONS.

Ppt. = precipitate. Filt. = filtrate. Sol. = solution.

〰 placed under a formula means that the compound represented is thrown down as a precipitate; when placed above, that it is given off as a gas.

QUALITATIVE ANALYSIS.

INTRODUCTION.

There are two principal divisions of analytical chemistry, viz., qualitative analysis and quantitative analysis.

The former, as its name implies, is an analysis or separation to determine the quality of an unknown substance, that is, the constituents contained in it. The object of quantitative analysis, on the other hand, is to determine the quantity of each of the various constituents present.

For an intelligent study of qualitative analysis it is very necessary that the student have some knowledge of general chemistry. In his work in the laboratory, order, neatness, and absolute cleanliness in regard to apparatus are very essential to success. Skill in manipulation comes naturally to some, and all may acquire it to a greater or less degree by practice.

The success of an analysis also depends very greatly on the care and forethought exercised by the student in performing the various operations that are called for in the course of his work. He should make it a rule never to attempt any test or separation until perfectly familiar with the conditions necessary for a successful performance of the operation in hand. Before adding any reagent, let him stop and ask himself the question, "Why do I add this, and what is it expected to do?" If he can answer this question, then let him use it in the way best suited to produce the desired result; if not, he should go no further until he understands fully the reasons for its use.

This is a common fault with very many students; they perform a certain operation in a certain way because their text-book says so, but further than that they know nothing about it, and are perfectly satisfied if by chance they get correct results. If they would only remember that the object in making all these tests and separations is to make them familiar with certain chemical facts and their application, they would perhaps realize that the first and most important point in any analysis is a thorough knowledge of the principles involved. Correct results will soon follow when this has been gained.

SECTION I.

THE METALS AND THEIR REACTIONS.

It has been found most convenient in analysis to treat the bases and acids separately.

In inorganic chemistry the bases comprise the metals, and the acids the non-metallic elements (with a few exceptions).

Experiment has shown that certain bases or acids act in the same manner when brought in contact with some particular substance of known composition. By making use of these substances, or reagents, as they are called, we are enabled to separate the metals and acids into groups. These groups can then be subdivided and separated into their several constituents. This grouping of the different elements is of great advantage, for it is obvious that if we add a group reagent and get no precipitate, the group of substances affected by this particular reagent cannot be present, and no further testing for them is necessary.

The classification of the bases adopted in this book is as follows·

First Group (Potassium, Sodium, and Ammonium).—These metals form very few insoluble compounds, and are not precipitated by any of the reagents used to throw down the metals of the other groups.

Second Group (Barium, Strontium, Calcium, and Magnesium).—This group is distinguished from the first by the insolubility of its normal carbonates and phosphates, as well as other salts, and from the succeeding groups by the fact that it is not precipitated by either hydrosulphuric acid or ammonium sulphide.

Third Group (Aluminium, Chromium, and Titanium).—These metals are not precipitated by hydrosulphuric acid from acid solution, and with ammonium sulphide in neutral solutions yield precipitates of hydroxide.

Fourth Group (Iron, Manganese, Zinc, Cobalt, and Nickel).—The metals of this group are not precipitated by hydrosulphuric acid from solutions acid with the mineral acids. Ammonium sulphide in neutral or alkaline solutions precipitates them as sulphides.

Fifth Group (Silver, Lead, Mercury, Bismuth, Copper, and Cadmium).—Precipitated as sulphides from alkaline, neutral, or acid solutions by hydrosulphuric acid. The precipitate is insoluble in ammonium sulphide.

Sixth Group (Tin, Antimony, Arsenic, Gold, and Platinum).—Precipitated by hydrosulphuric acid from acid solutions. The precipitate is soluble in ammonium sulphide, which distinguishes this group from the third, fourth, and fifth groups.

We might at once proceed to the separation of the metals into the different groups just mentioned, but this would be of no advantage until we know something of the individual characteristics of the various members of each group. Until these have been studied we are in no position to distinguish the several metals from each other. Before taking up this portion of our work it will be well, however, to give a little time to the explanation of certain terms that are frequently used, such as base, acid, etc.,* and to the study of chemical equations.

If we examine the two compounds hydrochloric acid (HCl) and potassium hydroxide (KOH) we find that they differ very decidedly from each other. The former has an acid or sour taste, and changes the color of many vegetable substances. The lat-

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For a more complete explanation of these terms see Remsen's *"Theoretical Chemistry."*

ter has an alkaline taste, and restores the color of vegetable substances that have been changed by the acid. Their characteristics in every way are opposed one to the other, and if they are brought together they neutralize each other, yielding a compound possessing none of the characteristics of either the acid or the hydroxide. These two compounds serve to represent the two great classes of compounds called acids and bases. Besides the two just mentioned, there are many others whose characteristics are equally distinct and which are easily placed in one class or the other. There are some substances, however, whose properties are not so decided and which act as acids towards some bases and like bases towards some acids.

Like hydrochloric acid, all acids contain hydrogen, which hydrogen is replaceable by a base. Some acids contain besides this hydrogen a certain part that is not so replaceable: such, for example, is acetic acid, $H(C_2H_3O_2)$, in which three of the hydrogen atoms cannot be replaced by metals.

In acids containing oxygen the acid hydrogen is supposed to be in combination with one of the oxygen atoms as hydroxyl (OH), and it is only the hydrogen so combined that is replaceable by bases. In sulphuric acid we have two hydroxyls and two replaceable hydrogen ($SO_2(OH)_2$ or H_2SO_4), in phosphoric acid three, in silicic acid four, etc.

Acids containing one replaceable hydrogen are called monobasic, those having two are said to be dibasic. There are besides these tribasic and tetrabasic acids.

Bases.—As already stated, the bases have properties just the reverse of the acids. Among the inorganic compounds they usually consist of hydroxyl in combination with a metal (except NH_4OH), as KOH, $NaOH$, $Ba(OH)_2$, etc.

The chief characteristic is their power of combining with acids to form neutral compounds.

Salts.—When an acid and a base act on each other they neutralize each other's properties to a greater or less extent. In the case already given of hydrochloric acid and potassium hydroxide we have a complete neutralization and the formation of a neutral substance possessing none of the characteristics of either the acid or the base. This substance is called a salt. Its formation may be represented by this equation:

$$KOH + HCl = KCl + H_2O.$$

In the case of a bibasic acid, such as sulphuric, we may get either a neutral or an acid salt:

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O;$$
$$KOH + H_2SO_4 = KHSO_4 + H_2O.$$

The first K_2SO_4 is called a neutral or normal salt. It is a salt formed by the displacement of all of the acid hydrogen of an acid by an equivalent amount of base. The second $KHSO_4$ is called an acid salt because it still contains hydrogen that may be replaced by a base.

Tri- and tetrabasic acids also form acid salts.

It is well to remember that normal salts are not always neutral to test-paper.

A strong acid in combination with a weak base gives a salt that turns blue litmus red, and a strong base in combination with a weak acid has the reverse effect, turning red litmus blue.

Besides normal and acid salts, there is still another class called basic salts. These are the reverse of the acid salts—that is, they contain a greater amount of base than there is acid to neutralize. Magnesium affords a good example of such a salt. The normal carbonate has the composition $MgCO_3$, but besides this it forms basic carbonates, as $4MgCO_3Mg(OH)_2$. This compound still contains basic hydroxyl, and for this reason it is called a basic salt.

We have already had occasion to use chemical formulas and equations, and a little time will now be given for a brief explanation of their significance.

CHEMICAL REACTIONS.

All chemical changes may be expressed by means of reactions written in the form of an equation, e.g.:

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl.$$

Now let us examine this equation and see what it is intended to express by it. In the first place it is a kind of shorthand for chemical names; instead of writing out the words "barium chloride" we denote it much more easily by using the chemical symbol belonging to each element contained in the compound. Thus in the example given Ba stands for barium and Cl for chlorine. Perhaps you may ask why we write it $BaCl_2$ and not simply BaCl. This brings us to another important property of symbols, viz., that they not only represent the elements themselves, but they also represent their atomic weights, as compared with the atom of hydrogen which is taken as the unit. Now in the example under discussion it has been found by quantitative analysis that it contains 137 parts by weight of barium and 71 parts of chlorine. The weight of the barium atom has been found to be 137 times that of the hydrogen atom, hence in this compound we have an amount of barium equal to one atom. The chlorine atom has been found to be 35.5 times as heavy as that of hydrogen, hence if $BaCl_2$ contains 71 parts of chlorine to one barium atom (137) it must contain $71 \div 35.5$ (weight of 1 atom of chlorine) equals 2 atoms of chlorine.

This we denote by writing the figure 2 at the lower right-hand corner of the symbol of the element; hence we see that $BaCl_2$ means in the first place the chemical compound barium chloride; secondly, that it represents definite weights of the constituent elements, and also the number of atoms of each element in the molecule, or at least their relative proportions.

When a number is written before the symbol representing a molecule, as $2NaCl$, it means two molecules.

If we should perform the chemical operation expressed by the equation given, we would find that 208 (Ba 137 + $Cl_2$71) parts by weight of barium chloride and 142 (Na_2 46 + S 32 + O_4 64) parts of sodium sulphate would produce 233 (Ba 137 + S 32 + O_4 64) parts of barium sulphate and 117 (2(Na 23 + Cl 35.5)) parts of sodium chloride.

It should be remembered in all equations representing chemical change, that the number of atoms on one side of the equation must be exactly equal to those on the other; nothing can be gained or lost.

Having gained some idea as to what an equation means, let us see if they differ from each other in any important respects.

In the equation cited it is evident that we have a simple interchange of the elements contained in the two substances used, the barium replacing the sodium and the sodium the barium. Such a transposition is called metathesis, and to this class of equations belong a very large number of chemical reactions.

It is a general rule, that if we mix two solutions capable of forming by exchange or transposition a compound insoluble in the mixture, such insoluble compound will be produced and precipitated. In the case just given, although $BaCl_2$ and Na_2SO_4 are both soluble in water, yet when we mix them $BaSO_4$ is precipitated, because it is insoluble in water.

Other forms of chemical change are those of combination or synthesis, as *

$$H_2 + Cl_2 = 2HCl,$$
$$2C + O_2 = 2CO;$$

those of dissociation or analysis, as

$$\begin{aligned} &CaCO_3 \text{ (on ignition)} &&= CaO + CO_2, \\ &2AuCl_3 \quad\quad \text{"} &&= 2Au + 3Cl_2; \end{aligned}$$

and those of oxidation and reduction, the latter two representing a very important series of reactions. Oxidation, strictly speaking, would mean an increase in the quantity of oxygen contained in a body, but the term is often used when oxygen takes no part in the work, as when $FeCl_2$ is changed to Fe_2Cl_6 by means of chlorine:

$$2FeCl_2 + Cl_2 = Fe_2Cl_6.$$

Although oxygen does not enter into the reaction, we say the $FeCl_2$ has been oxidized—meaning that it has been changed from a salt corresponding to FeO to one corresponding to Fe_2O_3.

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* Generally in these reactions there is dissociation as well as combination. In the example given the molecules of hydrogen, chlorine, and oxygen must split up into separate atoms before combining.

As an example of an oxidation equation let us take the one showing the oxidation of $FeSO_4$ to $Fe_2(SO_4)_3$ by $K_2Mn_2O_8$* and H_2SO_4:

$$5Fe_2(SO_4)_2 + K_2Mn_2O_8 + 8H_2SO_4 =$$
$$5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

In order to write such an equation as this, it is necessary to know, first, how much oxygen is needed to change the body from the lower oxide to the higher; second, how much oxygen we can get from each molecule of our oxidizing agent and what are the by-products formed by the reduction or decomposition of the latter; also what are the other products, if any, that are formed by the chemical changes going on. In order to determine the amount of oxygen necessary, we will first examine the composition of the body to be oxidized, $FeSO_4$.

Ferrous sulphate probably contains two atoms of iron in the molecule, as shown in the following graphic formulæ:

$$\begin{array}{l} Fe = O \\ \| \\ Fe = O \end{array} \quad \text{Ferrous Oxide} \qquad \begin{array}{l} Fe = SO_4 \\ \| \\ Fe = SO_4 \end{array} \quad \text{Ferrous Sulphate}$$

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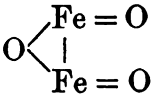
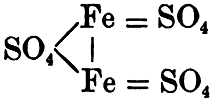
* Also written $KMnO_4$.

The composition of ferric sulphate, the product of the oxidation, is shown by the following formulæ:



Ferric oxide



Ferric sulphate.

On comparing the formula for ferrous oxide with that for ferric oxide, we see that in the reaction every molecule of the former has taken up one more atom of oxygen in order to become ferric oxide, or, in other words, the ferric oxide contains one more atom of oxygen in the molecule than does the ferrous; hence every atom of oxygen yielded by the oxidizing agent will oxidize one molecule of ferrous oxide (Fe_2O_2) to ferric oxide (Fe_2O_3).

Next let us see in what way the permanganate acts with the sulphuric acid. It has been found that it is decomposed or reduced, when in presence of an oxidizable substance, as shown in the following equation:

$$K_2Mn_2O_8 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5O + 3H_2O.$$

From this we see that every molecule of the $K_2Mn_2O_8$ will yield five atoms of oxygen, free to enter into combination with the iron, and we have already determined that each molecule of ferrous oxide (Fe_2O_2) requires one atom of oxygen to change it to ferric oxide (Fe_2O_3); hence five atoms of oxygen will oxidize five molecules of the Fe_2O_2 to Fe_2O_3. Next, how much H_2SO_4 will be needed besides that already contained in the ferrous sulphate. Ferric oxide when it combines with H_2SO_4 does so in the following manner:

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O.$$

Hence it is evident that for each molecule of Fe_2O_3 we shall need three of H_2SO_4; but as there are already two molecules present in the ferrous sulphate, we shall actually need but one more for every molecule of iron oxidized; and for five, the amount oxidized by one molecule of $K_2Mn_2O_8$, five H_2SO_4 will be required—making eight in all, with the three needed for combination with the potassium and manganese of the permanganate.

We have now determined the quantities of each reagent taking part in the reaction, and also the quantities of the products.

We will now take another reaction, in which at first sight the action of the oxidizing agent is not so plain. If we heat chromic hydroxide with a solution of sodium carbonate and bromine, the chromium will be oxidized to chromic acid, although, of course, the bromine itself contains no oxygen. Let us first write down the substances taking part in the reaction and the products formed:

$$Cr_2(OH)_6 + Na_2CO_3 + Br$$
$$= 2Na_2CrO_4 + NaBr + CO_2 + H_2O.$$

The substance to be oxidized, $Cr_2(OH)_6$, consists of $Cr_2O_3 + 3H_2O$; the result of the oxidation, Na_2CrO_4, consists of $Na_2O + CrO_3$. As the molecule of $Cr_2(OH)_6$ contains two atoms of chromium, we must, if all the chromium is oxidized, produce two molecules of Na_2CrO_4.

In Na_2CrO_4 the CrO_3 is the acid anhydride, and it has formed the salt by acting on Na_2CO_3 as follows:

$$Na_2CO_3 + CrO_3 = Na_2CrO_4 + CO_2.$$

We see, therefore, that the product of the oxidation is really CrO_3 and that the Na_2CrO_4 results from the action of the CrO_3 on Na_2CO_3. Now if we start with a molecule of Cr_2O_3 and obtain as a result of the reaction two molecules of CrO_3, it is evident, as shown by the following formulæ,

$$Cr_2O_3 = \begin{cases} 2Cr, \\ 3O, \end{cases} \qquad 2CrO_3 = \begin{cases} 2Cr, \\ 6O, \end{cases}$$

that the Cr_2O_3 has taken up three more atoms of oxygen in the change to $2CrO_3$; hence for every molecule of Cr_2O_3 oxidized we must have three more atoms of oxygen. How does the bromine furnish it? It has been found that Br in alkaline solution acts as follows when oxidizable matter is present:

$$3Na_2CO_3 + 3Br_2 = 6NaBr + 3CO_2 + 3O.$$

6 parts of bromine and 3 of sodium carbonate will thus give us sufficient oxygen for the oxidation of one molecule of $Cr_2(OH)_6$ to $2CrO_3$.

The $2CrO_3$ formed then combines with more of the sodium carbonate to form sodium chromate as shown already.

We will then need, besides the three molecules of carbonate that react with the bromine, two more to combine with the $2CrO_3$, making five in all. Hence the complete equation will be

$$Cr_2(OH)_6 + 5Na_2CO_3 + 3Br_2$$
$$= 2Na_2CrO_4 + 6NaBr + 5CO_2 + 3H_2O.$$

An equation representing oxidation generally represents reduction as well—reduction meaning just the reverse of oxidation. In the case just considered, of the oxidation of ferrous salts by permanganate, the latter is reduced—that is, loses oxygen and becomes manganous sulphate—while the iron salt is oxidized. Sulphurous acid is a strong reducing agent owing to the facility with which it takes up oxygen and becomes sulphuric acid. This is shown in its action on ferric salts; thus:

$$Fe_2(SO_4)_3 + SO_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4.$$

Stannous chloride ($SnCl_2$) is another active reducing agent. When added in excess to a solution of $HgCl_2$ it reduces the latter to metallic mercury; at the same time it is oxidized to $SnCl_4$; thus:

$$2HgCl_2 + 2SnCl_2 = 2Hg + 2SnCl_4.$$

Many more examples showing oxidation and reduction might be given, but sufficient have been shown to serve as types of all.

FIRST GROUP.

POTASSIUM, SODIUM, AND AMMONIUM.

Characteristics of the Group.—The chief characteristic of this group, analytically, is the fact that all its salts, with very few exceptions, are soluble in water. The normal carbonates of the group are the only ones of all the bases that are soluble in this menstruum. The solubility of the sulphides also serves to distinguish this group from all of the other groups except the second. The solubility of the hydrates is of great analytical importance, for owing to their exceedingly strong basic properties we are enabled to precipitate nearly all of the other metals as hydroxides, by the addition of one of these hydrates to a solution of the metal.

Solutions of the hydrates and of the carbonates turn red litmus blue and turmeric paper brown.*

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* Litmus is a weak vegetable acid, dissolving in water to a red liquid. Its salts are blue. Litmus paper is colored with the red solution of the acid or the blue solution of one of its salts.

POTASSIUM. At. wt. 39.1; sp. gr. 0.865.

Potassium is a white lustrous metal. It oxidizes very rapidly on exposure to the air, and if thrown on water it takes fire spontaneously, burning with a purple flame, and the water is found to have an alkaline reaction.

$$2K + 2H_2O = 2KOH + \widetilde{H_2}.$$

Potassium should always be kept covered with petroleum to protect it from the air.

Potassium hydroxide and its salts are not volatile at a dull red heat. As already stated, very few of them are insoluble, the only ones being the platinichloride, acid tartrate, silicofluoride, and potassium cobaltic nitrite. The first and second are the ones generally used as tests for potassium.

Potassium Platinichloride (K_2PtCl_6).—If hydrochloroplatinic acid be added to neutral or acid solutions of potassium salts, not too dilute, a yellow crystalline precipitate of the platinichloride is formed. Very dilute solutions are not precipitated. The test is best made by adding hydrochloroplatinic acid to the solution to be tested in sufficient quantity to give a yellow color, the solution is then evaporated on the water-bath nearly to dryness, and alcohol added; if any potassium is present it will be found as a yellow crystalline precipitate. In case sodium salts are present care must be taken not to carry the evaporation to complete dryness, for sodium forms with the platinic salt a corresponding compound containing water of crystallization, which is soluble in alcohol so long as it retains this water, but if it be driven out by carrying the evaporation too far, then the sodium platinichloride also remains as a yellow residue.

$$2KCl + H_2PtCl_6 = \underbrace{K_2PtCl_6} + 2HCl.$$

The precipitate is soluble in 110 parts of cold and in 19 of boiling water. In alcohol it is very much more insoluble, requiring 12,000 parts of absolute alcohol to dissolve it.

On ignition it leaves a residue of potassium chloride, and platinum.

Hydrogen Potassium Tartrate ($KHC_4H_4O_6$).—If tartaric acid be added to neutral or alkaline solutions (in the latter case the reagent must be added until the solution becomes acid) of potassium salts, a white crystalline precipitate of the acid tartrate is thrown down (*a*). The precipitate is soluble in the mineral acids (*c*) and in alkalis (*b*).

(*a*) $KCl + H_2C_4H_4O_6 = \underbrace{KHC_4H_4O_6} + HCl$;

(*b*) $\underbrace{KHC_4H_4O_6} + KOH = K_2C_4H_4O_6 + H_2O$;

(*c*) $\underbrace{KHC_4H_4O_6} + HCl = KCl + H_2C_4H_4O_6$.

Equations *a* and *c* are apparently contradictory, but this is explained by the fact that in the test *a* the tartaric acid is added in excess (that is, more than sufficient to combine with the potassium), and in *c* the hydrochloric acid predominates. However, owing to the solubility of the precipitate in hydrochloric acid, the reaction as given in *a* is never complete, some of the potassium always remaining in solution. For this reason it is better to use as the precipitant a solution of hydrogen sodium tartrate, which forms in the reaction sodium chloride instead of hydrochloric acid. The sodium chloride has very little, if any, solvent action on the precipitate:

$$KCl + NaHC_4H_4O_6 = \underbrace{KHC_4H_4O_6} + NaCl.$$

Whichever precipitant is used, the solution should be concentrated and cold. Vigorous shaking helps the precipitation very much.

At 10° C. one part of the precipitate requires 250 parts of water to dissolve it, but it is soluble in 15 parts of boiling water.

Flame Test.—If a drop of a potassium salt (best the chloride or sulphate) on the loop of a platinum wire be held in the outer flame of the Bunsen burner the flame will be colored violet. The presence of sodium salts prevents the color from being seen.

By interposing between the flame and the eye a piece of deep cobalt-blue glass or an indigo prism the yellow sodium flame is cut off and the violet of the potassium is visible.

SODIUM (Na). At. Wt. 23; sp. gr. .972.

Sodium is a soft silver-white metal greatly resembling potassium in all its properties. The properties of the hydroxide and its salts closely resemble the corresponding potassium compounds, with very few exceptions. The sodium salts are even more soluble, there being only one that is at all insoluble in water, viz., the pyroantimonate.

Sodium Pyroantimonate.—If a freshly prepared solution of potassium pyroantimonate* be added to a moderately concentrated solution of a sodium salt having a neutral or slightly alkaline reaction, a white crystalline precipitate of sodium pyroantimonate is thrown down more or less quickly, depending on the concentration of the liquid. By making the test in a watch-glass and stirring thoroughly with a glass rod the formation of the precipitate is much hastened.

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* Prepared by dissolving a little of the solid salt in hot water and filtering from any insoluble residue.

Acid solutions should always be evaporated to dryness, if possible, to remove the free acid, or if this cannot be done they should be neutralized with potassium hydroxide or carbonate. Free acid decomposes potassium pyroantimonate, giving a white amorphous precipitate of metantimonic acid ($HSbO_3$).

In making this test no other salts than those of potassium and sodium should be present.

In dilute solutions the precipitate will not form for a long time, often as much as 12 hours being required.

Sodium pyroantimonate is soluble in 300 parts of boiling water. The following equation represents its formation:

$$2NaCl + K_2H_2Sb_2O_7 = \underbrace{Na_2H_2Sb_2O_7} + 2KCl.$$

Flame Test.—Sodium salts impart to the Bunsen flame an intense yellow color, even when present in very minute quantity. The presence of potassium salts does not interfere with this test.

It must be remembered that the merest trace of sodium salt will color the flame yellow. Simply touching the platinum wire with the fingers is sufficient to give a decided test. If the sodium compound is present in appreciable quantity it gives a color to the flame that does not disappear quickly.

SCIENCE DEPARTMENT
THE STUYVES[illegible]
345 EAST
1 64
NEW YORK CITY

AMMONIUM (NH_4).

Ammonium is known only in combination (e.g., NH_4Cl). Ammonia, NH_3, is a gas at ordinary temperatures, and is very soluble in water. In this solution it is supposed to exist as the hydroxide NH_4OH. On heating the solution the ammonia is set free again as gas.

Ammonia combines with all the acids to form ammonium salts, e.g.:

$$NH_3 + HCl = NH_4Cl;$$
$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

All ammonium salts are volatile at a low red heat, which is a distinction between them and sodium and potassium salts, the two latter not being volatilized at that temperature.

The solubility of the ammonium salts corresponds very closely with those of potassium, the only difficultly soluble ones being the platinichloride, the acid tartrate, and certain mercurammonium compounds.

Liberation of Ammonia Gas.—The most characteristic test for ammonium compounds depends on the fact that they easily evolve ammonia (NH_3) when treated with suitable reagents.

If an ammonium salt be triturated with slacked lime and a few drops of water, or heated with solution of sodium or potassium hydroxide, ammonia gas is set free (*a* and *b*), which may be recognized by its pungent odor, by turning moistened red litmus paper blue, and by the dense white fumes formed when brought in contact with any volatile acid, as hydrochloric, nitric, or acetic (*c*). This last test is best made by moistening a glass rod with a drop or two of the acid and holding it over the test-tube or other vessel in which the experiment is being made. Hydrochloric acid is the most sensitive in this way, but it must be remembered that the concentrated acid itself fumes in moist air. For this reason, acetic acid is more reliable.

Another very delicate test for free ammonia is to moisten a piece of filter-paper with mercurous nitrate and hold this over the test-tube or beaker in which the ammonia is being evolved. The paper will become black or gray, owing to the action of the ammonia on the mercurous salt (*d*).

(*a*) $2NH_4Cl + Ca(OH)_2$

$$= CaCl_2 + \overbrace{2NH_3} + 2H_2O;$$

(*b*) $NH_4Cl + KOH = KCl + \overbrace{NH_3} + H_2O;$

(*c*) $NH_3 + HCl = NH_4Cl;$

(*d*) $Hg_2(NO_3)_2 + 2NH_3$

$$= \underbrace{NH_2Hg_2NO_3}\text{ (black)} + NH_4NO_3.$$

Presence of other bases does not interfere with the liberation of ammonia from its compounds by the hydroxides of the alkalis or alkaline earths.

Ammonium Platinichloride.—Hydrochloroplatinic acid precipitates ammonium salts under the same conditions as for potassium salts, giving a yellow crystalline precipitate, which is rather more insoluble than the potassium platinichloride. On ignition (best after addition of ammonium oxalate) it leaves a residue of metallic platinum (distinction from the potassium salt).

$$2NH_4Cl + H_2PtCl_6 = \underbrace{(NH_4)_2PtCl_6} + 2HCl.$$

Hydrogen Ammonium Tartrate.—Hydrogen sodium tartrate added to concentrated solution of ammonium salts gives a white crystalline precipitate of hydrogen ammonium tartrate. Tartaric acid precipitates only very concentrated solutions. The precipitate is much more soluble than the corresponding potassium salt.

$$NH_4Cl + NaHC_4H_4O_6 = \underbrace{(NH_4)HC_4H_4O_6} + NaCl.$$

Dimercurammonium Iodide.—For all ordinary tests the reactions already given are sufficient, but in cases where it is necessary to test for exceedingly minute quantities of ammonia (as in potable waters) the Nessler test, as it is called, is the most delicate. This is made in the following manner: To the solution containing free ammonia or an ammonium salt is added a solution of potassium mercuric iodide containing an excess of potassium hydrate (Nessler reagent*). If the ammonia is present in any quantity a brown precipitate is formed, but in very dilute solutions it gives only a brown or yellow color.

$$\begin{aligned}&2(2KI, HgI_2) + NH_3 + 3KOH \\ &\qquad = NHg_2I, H_2O + 7KI + 2H_2O.\end{aligned}$$

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* Nessler's reagent is made by dissolving 16 grams of mercuric chloride in about 500 c.c. of water. Add this slowly to a solution of 35 grams of potassium iodide in 200 c.c. of water, until a precipitate begins to form. Then add 160 grams of potassium hydrate and dilute to one litre. Finally, add strong solution of mercuric chloride until the red precipitate of mercuric iodide just begins to be permanent. Do not filter, but allow any precipitate to settle.

The presence of salts of the alkalies (except cyanides and sulphides) does not interfere with this test, but care must be taken to see that the solution is neutral or alkaline before adding the reagent. Salts of the alkaline earths should be removed by adding just sufficient of a mixture of about 1 part potassium or sodium hydrate and 2 parts of sodium carbonate to completely precipitate them. The precipitate is allowed to settle and the clear liquid tested with the Nessler reagent.

SEPARATION OF FIRST-GROUP METALS.

We have found by our study of the several metals of the group that potassium and ammonium salts are both precipitated by hydrochloroplatinic acid and hydrogen sodium tartrate, so we cannot use these reagents as a distinctive test for either metal when both may be present in the same solution. Again, the test for sodium with pyroantimonate requires that no other salts than those of potassium may be present, and as it adds potassium to the solution, we cannot, of course, test in it for that metal.

It is evident, then, that the first step in the separation will be to determine whether ammonium salts are present, and if found, to remove them by suitable means.

The test with slaked lime or potassium or sodium hydrates affords us a ready means of testing for ammonia, the test being made on a separate portion of the mixture. If found, we can make use of the fact that ammonium salts are volatile on ignition, by taking a fresh portion of the solution and evaporating to dryness and then igniting carefully until no more fumes of ammonia salts are given off. The residue will now contain only the sodium and potassium salts, and by dissolving it in a very little water and dividing into two portions we can test one with pyroantimonate for sodium and the other with hydrochloroplatinic acid or hydrogen sodium tartrate for potassium.

It is well to test the residue left after driving out the ammonium salts by taking a little of it on a platinum wire and making the flame test. This simple test will often show at once which metal is present; for instance, if it should give a violet flame, this would prove the presence of potassium, and it would be unnecessary to look further for sodium, as its flame would have shown even in presence of much potassium. If the residue gave a strong yellow flame that took some time to burn off, that would be sufficient for sodium, and the potassium could then be determined by use of the blue glass or by precipitation with hydrochloroplatinic acid.

SECOND GROUP.

BARIUM, STRONTIUM, CALCIUM, MAGNESIUM.

The insolubility of the normal carbonates and phosphates of this group serve to distinguish it from the first group, and the fact that it is not precipitated by hydrosulphuric acid nor ammonium sulphide distinguishes it from the succeeding groups.

The solubility of the hydroxides in water decreases in regular order from barium hydroxide, which is easily soluble to magnesium hydroxide, which is very insoluble. The reverse is true of the sulphates, magnesium sulphate being easily soluble, calcium sulphate difficultly so, strontium sulphate much more insoluble, and barium sulphate insoluble not only in water but in acids.

The hydroxides and salts of this group are all colorless (unless the acid be colored as chromic acid), and are not volatile at a red heat.

BARIUM (Ba). At. wt. 137.4.

Barium is found in considerable quantities as barite or heavy spar ($BaSO_4$) and as witherite ($BaCO_3$).

Almost all of the barium salts are insoluble in water, but with the exception of the sulphate and silicofluoride they are soluble in acids. The chloride and nitrate are nearly insoluble in alcohol, and insoluble in a mixture of equal parts of alcohol and ether. They are also insoluble in strong hydrochloric or nitric acids; for this reason, if either of these acids be added to a concentrated solution of a barium salt a white precipitate will form, which, however, dissolves readily on diluting with water.

Barium Hydroxide ($Ba(OH)_2$).—Sodium and potassium hydrates (free from carbonate) give no precipitate with barium salts unless the solutions are concentrated.

Ammonium hydrate causes no precipitate.

Barium Carbonate ($BaCO_3$).—The carbonates of potassium, sodium, and ammonium precipitate barium salts as a white amorphous precipitate. The precipitate is slightly soluble in ammonium chloride. It is easily soluble in all acids.

$$BaCl_2 + (NH_4)_2CO_3 = \underbrace{BaCO_3} + 2NH_4Cl;$$

$$\underbrace{BaCO_3} + 2HC_2H_3O_2 = Ba(C_2H_3O_2)_2 + \overbrace{CO_2}.$$

Barium Sulphate (*$BaSO_4$*).—Sulphuric acid or soluble sulphates give, even in very dilute solutions of barium salts, a white pulverulent precipitate of barium sulphate. The precipitate is insoluble in water and dilute acids.

A solution of calcium sulphate in water serves as a useful reagent to distinguish between barium and strontium salts. With the former it gives an immediate precipitate, unless the solution be very dilute, but with strontium the precipitate forms only slowly.

$$BaCl_2 + H_2SO_4 = \underbrace{BaSO_4} + 2HCl;$$
$$BaCl_2 + CaSO_4 = \underbrace{BaSO_4} + CaCl_2.$$

Barium Chromate (*$BaCrO_4$*).—Solutions of barium salts containing no free mineral acid are precipitated by potassium chromate or dichromate, giving a yellow precipitate which is very insoluble in water and in ammonia. It is slightly soluble in ammonia salts, in chromic acid, and acetic acids. The solubility in acetic acid increases with the strength of the acid.

$$BaCl_2 + K_2CrO_4 = \underbrace{BaCrO_4} + 2KCl.$$

Soluble phosphates and oxalates precipitate neutral or alkaline solutions of barium salts as white precipitates of phosphate (*a*) and oxalate (*b*). The phosphate is soluble in hydrochloric, nitric, and acetic acids, the oxalate in hydrochloric and nitric acids, but not in acetic except when first precipitated.

$$(a) \quad BaCl_2 + Na_2HPO_4 = \underbrace{BaHPO_4} + 2NaCl;$$

$$(b) \quad BaCl_2 + (NH_4)_2C_2O_4 = \underbrace{BaC_2O_4} + 2NH_4Cl.$$

Flame.—Barium salts (best the chloride or sulphate) when held in the Bunsen flame on a loop of platinum wire impart to it a yellowish-green color.

STRONTIUM (Sr). At. wt. 87.6.

Strontium salts in their reactions very closely resemble the corresponding barium compounds.

The hydroxide is somewhat less soluble in water than barium hydroxide. The chloride is deliquescent, and is soluble in absolute alcohol (distinction from barium). The nitrate is nearly insoluble in absolute alcohol and in a mixture of absolute alcohol and ether (distinction from calcium).

The hydroxides and carbonates of the alkalies give the same reactions with strontium salts as with those of barium.

Strontium Sulphate (*$SrSO_4$*).—Sulphuric acid and soluble sulphates precipitate strontium salts, giving a white precipitate of sulphate. The precipitate is much more soluble than barium sulphate, both in water and in acids, and for this reason it precipitates only slowly from dilute solutions. With calcium sulphate the precipitation is always slow except in very concentrated solutions (distinction from barium). The application of heat helps this precipitation as well as all others of strontium as sulphate.

Soluble phosphates and oxalates precipitate neutral or alkaline solutions of strontium salts, yielding white precipitates of phosphate and oxalate corresponding to the barium phosphate and oxalate, and having about the same solubilities.

Potassium dichromate does not precipitate strontium salts even from concentrated solutions. Normal chromates in neutral solutions not very dilute give, on standing for some time, a yellow precipitate of chromate. Solutions acid with acetic acid are not precipitated (distinction from barium).

Flame.—Strontium salts (preferably the chloride) impart a crimson color to the Bunsen flame that is very characteristic. Strontium sulphate and salts of fixed acids should be moistened with concentrated hydrochloric acid before bringing them into the flame.

CALCIUM (Ca). At. wt. 40.

Calcium is found in enormous quantities in the form of carbonate (limestone, marble, etc.) and as sulphate (gypsum), and is an important constituent of many silicates.

Calcium oxide (quicklime) and the hydroxide $Ca(OH)_2$ (slaked lime) are considerably more insoluble than barium and strontium oxides and hydroxides. Calcium chloride and nitrate are soluble in absolute alcohol and in a mixture of alcohol and ether.

The hydroxides of potassium, sodium, and ammonium, and their carbonates, act in much the same way with calcium salts as with those of barium and strontium.

Calcium carbonate when first precipitated is amorphous, but on standing, or more quickly by heating, changes to the crystalline form. It is easily soluble in acids, even in carbonic, and is also somewhat soluble in ammonium chloride. From its solution in carbonic acid it is precipitated on heating.

$$CaCl_2 + Na_2CO_3 = \underbrace{CaCO_3} + 2NaCl;$$

$$\underbrace{CaCO_3} + CO_2 + H_2O = CaH_2(CO_3)_2;$$

$$CaH_2(CO_3)_2 + \text{heat} = \underbrace{CaCO_3} + \overbrace{CO_2} + H_2O.$$

Calcium Sulphate.—Sulphuric acid and soluble sulphates give with calcium salts white precipitates of sulphate that form more or less quickly, according to the sulphate used and the strength of the solution.

Very dilute solutions are not precipitated.

Calcium sulphate is soluble in a large quantity of water, and much more soluble in acids. It is also soluble in strong solution of ammonium sulphate.

Calcium Oxalate.—Solutions of calcium salts containing no free mineral acid are precipitated by ammonium oxalate, yielding a white precipitate of oxalate. In very dilute solutions the precipitate only forms slowly. Presence of free ammonia and heat help the precipitation. Calcium oxalate is easily soluble in hydrochloric and nitric acids, and almost insoluble in acetic or oxalic. Of all tests for calcium it is the most delicate.

Soluble phosphates give the same reactions with calcium salts as with those of barium and strontium.

Potassium dichromate and the normal chromates do not precipitate calcium salts.

Flame.—Calcium salts give a yellowish-red color when brought into the Bunsen flame.

MAGNESIUM (Mg). At. wt. 24.3; sp. gr. 1.74.

Magnesium is a silvery-white metal, which when ignited in the air burns with an intense white flame, forming the oxide MgO.

It does not decompose water at ordinary temperatures. It is found widely distributed in nature as carbonate and silicate. Hydrochloric and sulphuric acids dissolve it very readily with evolution of hydrogen.

The oxide and hydroxide are very insoluble in water, but soluble in acids.

Many magnesium salts are soluble in water, and with the exception of the sulphate are easily decomposed on gentle ignition, most of them even by evaporation of their solutions.

Magnesium Hydroxide. — The hydroxides of potassium, sodium, barium, strontium, and calcium give, with solutions of magnesium salts, a white precipitate of hydroxide. If ammonium salts are present, the reagent must be added in excess and the solution boiled to insure complete precipitation:

$$MgCl_2 + 2KOH = \underbrace{Mg(OH)_2} + 2KCl.$$

Ammonium Hydrate.—The action of ammonia on magnesium salts varies, depending on the presence or absence of ammonium salts. Magnesium salts readily unite with those of ammonium to form double salts, and on these compounds ammonia has no action. Of course the addition of ammonia to an acid solution containing magnesium has the same effect, as the first action is a combination of the ammonia and free acid forming an ammonium salt, which then unites with the magnesium to form the double salt.

When ammonium salts or free acid are not present, ammonia partially precipitates magnesium solutions, giving a white precipitate of the hydroxide:

$$2MgCl_2 + 2NH_4OH = \underbrace{Mg(OH)_2}_{} + MgCl_2, NH_4Cl + NH_4Cl.$$

The reason for the precipitation not being complete is shown by the equation to be due to a portion of the magnesium uniting with the ammonium chloride formed in the reaction and producing the double chloride $MgCl_2, NH_4Cl$.

The magnesium hydroxide formed in this and the preceding reaction is soluble in ammonium salts, as shown by the following reaction:

$$Mg(OH)_2 + 3NH_4Cl = MgCl_2, NH_4Cl + 2NH_4OH.$$

Magnesium Carbonate.—Sodium and potassium carbonates give with magnesium solution a white precipitate of basic carbonate, a portion of the magnesium remaining in solution as acid or bicarbonate. On heating the solution the latter is decomposed and precipitates as normal carbonate:

$$5MgCl_2 + 5Na_2CO_3 + H_2O = \underbrace{4MgCO_3, Mg(OH)_2}_{} + 10NaCl + \overbrace{CO_2}^{}.$$

The presence of ammonium salts interferes with or prevents this precipitation.

Ammonium Carbonate in presence of ammonium chloride does not precipitate magnesium salts unless the latter are concentrated, and then only after standing some time.

In absence of ammonium salts it gives after some time a precipitate of $MgCO_3 3H_2O$ if the ammonium carbonate be present in slight excess; of a double carbonate, $MgCO_3, (NH_4)_2CO_3, 4H_2O$, when the reagent is added in large excess.

Magnesium Phosphate.—Hydrogen disodium phosphate gives with neutral solutions of magnesium salts a white precipitate of phosphate, $MgHPO_4$:

$$MgCl_2 + Na_2HPO_4 = \underbrace{MgHPO_4} + 2NaCl.$$

The test is made much more delicate by adding ammonium chloride and hydrate to the solution before the addition of the phosphate. Under these conditions a white crystalline precipitate of magnesium ammonium phosphate is thrown down, even from very dilute solutions. The presence of free ammonia in excess helps the precipitation. Shaking or stirring the mixture hastens the precipitation:

$$\begin{aligned} &MgCl_2 + NH_4Cl + NH_4OH + Na_2HPO_4 \\ &\qquad = \underbrace{MgNH_4PO_4} + 2NaCl + NH_4Cl + H_2O. \end{aligned}$$

The precipitate of $MgHPO_4$ and that of $MgNH_4PO_4$ are both easily soluble in acids, even in acetic.

Ammonium Oxalate in dilute solutions of magnesium salts causes no precipitate except on standing. In concentrated solutions a precipitate forms more quickly. Presence of ammonium chloride and hydrate interferes with or prevents the precipitation of magnesium as oxalate.

Sulphuric Acid and Soluble Sulphates produce no precipitate with magnesium salts.

Chromates do not precipitate magnesium solutions.

Magnesium salts do not give any color to the Bunsen flame.

SEPARATIONS.

On reviewing the reactions of the metals of the second group we find that three of them, viz., barium, strontium, and calcium, act in much the same way with many of the reagents, and consequently the methods of separation are correspondingly limited. The metals just mentioned are readily separated from magnesium by making use of the action of ammonium carbonate in presence of ammonium chloride, which precipitates them as carbonates, leaving the magnesium in solution. The carbonates may then be separated from each other by taking advantage of the differences in their reactions with chromates and by the difference in solubility of strontium and calcium sulphates. The accompanying scheme of separation is based on these reactions.

Another method, and one which has the advantage of giving some idea as to the quantity of each metal present, is to dissolve the three carbonates in acetic acid and precipitate the barium as in the method given in the scheme; the strontium and calcium are then reprecipitated from the filtrate by adding ammonia and ammonium carbonate. The carbonates are dissolved in nitric acid and evaporated to dryness, and then heated for about fifteen minutes at a temperature of 150° to 180° C.

The dry residue should be at once finely pulverized and then rubbed up with about 10 c.c. of a mixture of equal parts of absolute alcohol and ether. The solution is filtered after a few minutes and the residue washed several times with small quantities of the alcohol and ether mixture. The strontium nitrate remains insoluble while the calcium nitrate goes into the solution. The residue may be dissolved in a little water and the presence of strontium confirmed by testing with calcium sulphate. The solution containing the calcium nitrate is tested by the addition of a few drops of dilute sulphuric acid, when the formation of a precipitate in any considerable quantity proves the presence of calcium. Should the precipitate be only trifling, it might possibly be due to a trace of strontium, and it should be tested in the flame or by some other confirmatory test.

The Sulphates of Barium, Strontium, and Calcium are so insoluble in both water and acids (this is especially the case with barium and strontium sulphates) that some special method has to be adopted in order to get them into solution. This is best done by fusing the dry sulphates with four or five parts of sodium potassium carbonate in a platinum crucible. The insoluble sulphates are thus converted into carbonates, and the sulphuric acid combines with the sodium and potassium as sulphates soluble in water:

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4.$$

By treating the fused mass with boiling water until thoroughly disintegrated the sodium and potassium sulphates, *as well* as the excess of flux, are dissolved, and on filtering and washing the residue (the washing should be continued until the washings give no precipitate with barium chloride) the carbonates of barium, strontium, and calcium are obtained free from sulphate, and can be at once dissolved in acetic acid and separated in the usual way.

SCHEME I.—SEPARATION OF 1° AND 2° GROUPS.

FILTRATE 23.

Add a small quantity of NH_4Cl, and then NH_4OH until alkaline, then $(NH_4)_2CO_3$ in slight excess; warm and filter. Wash the ppt. Note 1.

PPT. 35.

$BaCO_3 + SrCO_3 + CaCO_3$.

Dissolve in the least possible quantity of hot, dil. $HC_2H_3O_2$ (36), and test a small portion of the sol. for Ba, by addition of $CaSO_4$. An immediate ppt. shows Ba. If no ppt. forms at once heat gently and allow to stand 10 min. The appearance of a ppt. on standing will indicate Sr.

If Ba has been found by the above test, add to the main part of the sol., K_2CrO_4* in slight excess; allow to stand a few minutes, filter and wash. (If Ba is not found as above, omit this treatment, and proceed to test for Sr and Ca, as below, Part 1° and 2°. (Note 2.)

FILTRATE 35.

$MgCl_2$, $NH_4Cl + KCl + NaCl +$ traces of Ba and Ca $+ NH_4$ Salts.

Divide into 2 parts.

PART 1°.—Add a few drops of $(NH_4)_2SO_4$, and of $(NH_4)_2C_2O_4$; a white ppt. shows traces of $BaSO_4 + CaC_2O_4$ (43). Filter. To the filtrate add NH_4OH and Na_2HPO_4. A white, crystalline ppt. shows $MgNH_4PO_4$ (44), and proves Mg. (Note 3.)

PART 2°.—Evaporate to dryness, and ignite, to expel all NH_4 salts. Dissolve residue (45) in a little water, and filter. Evaporate the filtrate to very small bulk, and make the flame-test for Na. Then add a few drops of H_2PtCl_6 to the solution, and stir with a glass rod. A yellow, crystalline ppt. shows (46) K_2PtCl_6, and proves K. Addition of alcohol increases the delicacy of this test. (Note 4.)

PPT. 37.

$BaCrO_4$ (yellow).

FILTRATE 37.

$Sr(C_2H_3O_2)_2 + Ca(C_2H_3O_2)_2$.

Add NH_4OH to alkaline reaction, then $(NH_4)_2CO_3$ in slight excess, heat, filter, and wash.

PPT. 38.

$SrCO_3 + CaCO_3$.

Dissolve in hot dil. $HC_2H_3O_2$. Divide solution into two parts.

FILT. 38.

NH_4 salts.

Reject.

PART. 1°.

Add a solution of $CaSO_4$, warm and allow to stand some time. A white ppt. = $SrSO_4$. Moisten ppt. with HCl (conc.) and test in the flame. Crimson flame proves Sr.

PART 2°.

Make alkaline with NH_4OH, then add a concentrated solution of $(NH_4)_2SO_4$ boil for some minutes and filter. (Note 5.)

PPT. 41.

$SrSO_4 + CaSO_4$. (?)

FILTRATE 41.

Add a few drops of $HC_2H_3O_2$ & $(NH_4)_2C_2O_4$. A white ppt. $= CaC_2O_4$—proves Ca. (Note 6.)

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* Prepared from $K_2Cr_2O_7$ by adding NH_4OH until the color changes to yellow, but not sufficient to make the solution alkaline.

NOTES TO SCHEME.

Note 1.—The amount of ammonium chloride added must be sufficient to form a double chloride with the magnesium present, so that the latter will not be precipitated by the ammonia or ammonium carbonate. A large excess of the chloride is to be avoided, as the carbonates of barium and calcium are perceptibly soluble in it. When the solution under examination is a filtrate from the separation of the 3° and 4° groups, it is not necessary to add any ammonium chloride at this point because it has already been added before precipitating those groups. After the addition of the ammonia and ammonium carbonate the mixture should be heated gently (do not boil) for some time, and until the precipitate, if any, settles in the crystalline form.

If the solution is a filtrate from the 3° and 4° groups it is sometimes brown or almost black, due generally to an imperfect separation of nickel in

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the preceding groups. In such cases the solution should be boiled until no more ammonia is given off, then allowed to cool, and finally made slightly acid with acetic acid, and filtered. The precipitate is tested for nickel, and the filtrate, after being made alkaline with ammonia, for the 1° and 2° groups.

Ammonia is always tested for in the *original* solution. The test is made, as already described under the reactions for ammonia, by heating with an excess of sodium or potassium hydrate.

The formation of a precipitate on the addition of the alkali does not interfere with the test, but care must be taken to add sufficient of the hydrate to make the solution distinctly alkaline.

NOTE 2.—The precipitate of the carbonates should be dissolved in a little hot acetic acid and the solution obtained evaporated nearly to dryness to drive off any excess of acid.

It is then diluted with a small quantity of water and tested as given in the scheme. The presence of a little free acetic acid is necessary to prevent any strontium being thrown down as chromate, but an excess is injurious, as barium chromate is somewhat soluble in it.

NOTE 3.—If barium and calcium have not been found in Ppt. 35, the ammonium sulphate and oxalate should be added to separate portions of the filtrate, and if either or both give a precipitate they should be filtered on separate filters and the precipitates, after moistening with a drop of concentrated hydrochloric acid, tested on platinum wire in the Bunsen flame for barium and calcium. The ammonium sulphate, of course, precipitates the barium, and the oxalate the calcium and perhaps barium.

NOTE 4.—If magnesium has been found in part 1°, it is well to add some ammonium oxalate to part 2° before evaporation, as it helps to decompose the magnesium salt. The ignition must be continued until all fumes have ceased.

Should no precipitate form on addition of the hydrochloroplatinic acid, the solution must be evaporated nearly to dryness and alcohol added. Potassium, if present, will then surely show.

In using the flame test for sodium the student must learn to distinguish between a mere trace and any appreciable quantity.

NOTE 5.—This treatment with ammonium sulphate does not effect a complete separation of the strontium and calcium. Some of the calcium *generally remains* with the strontium, and a little of the strontium may dissolve and go into the solution with the calcium.

NOTE 6.—The solution is made slightly acid with acetic acid so as to prevent the precipitation of any traces of strontium that may have dissolved in the ammonium sulphate. If the solution is very dilute, the precipitate of calcium oxalate will only form slowly.

THIRD GROUP.

ALUMINIUM, CHROMIUM, TITANIUM.

THE oxides and hydroxides of this group are very insoluble in water. The precipitated hydroxides (except metatitanic acid) are easily soluble in acids; but the oxides dissolve with more or less difficulty, and after ignition are almost insoluble.

The third-group metals do not form sulphides in the wet way, and for this reason are not precipitated as sulphide by either hydrosulphuric acid (H_2S) or alkaline sulphides. Ammonium sulphide precipitates them from neutral solutions as hydroxide. This reaction distinguishes them from the metals of the fourth, fifth, and sixth groups.

ALUMINIUM (Al). At. wt. 27.1; sp. gr. 2.58.

Aluminium is found in enormous quantities in combination with silica, as clay, feldspar, etc. It also occurs as the oxide and fluoride. It is a moderately hard tin-white metal, very malleable and ductile, and may be highly polished. It fuses at 700° C. It is not oxidized by the air, and is unacted on by hydrosulphuric acid or ammonium sulphide. Nitric acid has scarcely any effect on it, but it is soluble in hydrochloric and sulphuric acids, and in sodium and potassium hydrates:

$$2Al + 6HCl = Al_2Cl_6 + \widetilde{3H_2};$$
$$2Al + 2KOH + 2H_2O = K_2Al_2O_4 + \widetilde{3H_2}.$$

Aluminium forms the oxide Al_2O_3 and a corresponding series of salts. The oxide dissolves with difficulty in dilute acids, but more easily when the acid is concentrated and hot. When fused with sodium or potassium disulphate it is converted into the sulphate, which is easily soluble in water:

$$Al_2O_3 + 3(K_2SO_4, SO_3) = Al_2(SO_4)_3 + 3K_2SO_4.$$

When fused with sodium or potassium hydrate or carbonate (if sodium or potassium hydrate is used the fusion must be made in a silver or nickel crucible) it forms an aluminate soluble in water or acids:

$$Al_2O_3 + 2KOH = K_2Al_2O_4 + H_2O.$$

The aluminium salts are almost all colorless. The haloid salts and the normal nitrate, sulphate, and acetate are all soluble in water. On ignition the soluble oxygen salts are decomposed, leaving a residue of oxide (Al_2O_3).

Many aluminium salts combine with those of the metals to form double salts, among the most important of which are the alums, such as $K_2SO_4, Al_2(SO_4)_3, 24H_2O$.

Most of the aluminium compounds insoluble in water (with the exception of certain minerals) are dissolved by hydrochloric acid.

Those that are insoluble in this acid may be got into a soluble form by fusion with alkaline hydrate, carbonate, or disulphate, as already explained.

Aluminium Hydroxide ($Al_2(OH)_6$).—If ammonium sulphide be added to a solution of an aluminium salt a white precipitate of the hydroxide is thrown down, which is insoluble in an excess of the precipitant:

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O \\ = Al_2(OH)_6 + 3(NH_4)_2SO_4 + \overbrace{3H_2S}.$$

Potassium and Sodium Hydroxides give with aluminium salts a precipitate of the hydroxide containing alkali and basic salt (*a*). The precipitate is easily soluble in excess of the reagent (*b*), and is not reprecipitated on boiling (distinction from chromium); but on the addition of ammonium chloride, especially on heating, it reprecipitates as the hydroxide (*c*).

$$(a)\ Al_2(SO_4)_3 + 6KOH = \underbrace{Al_2(OH)_6} + 3K_2SO_4;$$

$$(b)\ \underbrace{Al_2(OH)_6} + 2KOH = K_2Al_2O_4 + 4H_2O;$$

$$\begin{aligned}(c)\ K_2Al_2O_4 + 2NH_4Cl + 4H_2O\\ = \underbrace{Al_2(OH)_6} + 2KCl + 2NH_4OH.\end{aligned}$$

Ammonium Hydroxide also gives a precipitate of the hydroxide which is insoluble in a slight excess of the precipitant, but perceptibly soluble in a large excess. From this solution in excess of the ammonia it is reprecipitated on boiling, as this drives out the excess of ammonia.

The Alkali Carbonates give a precipitate of hydroxide and basic carbonate. The precipitate is slightly soluble in the carbonates of potassium and sodium, but much less soluble in ammonium carbonate.

Barium Carbonate completely precipitates solutions of aluminium salts, even in the cold, giving a precipitate consisting of hydroxide and basic salt. The barium carbonate should be used in a very finely divided state.

The presence of non-volatile organic acids, such as tartaric, citric, etc., and of sugar or similar organic matter, interferes with or completely prevents the precipitation of aluminium as hydroxide.

Aluminium Phosphate.—With neutral solutions of aluminium salts or those acid only with acetic acid sodium phosphate gives a white flocculent precipitate of phosphate.

The precipitate is soluble in the mineral acids and in sodium or potassium hydroxide, but difficultly so in ammonia. Ammonium chloride reprecipitates it from its solution in the alkalies:

$$Al_2(SO_4)_3 + 2Na_2HPO_4 + 2NaC_2H_3O_2$$
$$= \underbrace{Al_2(PO_4)_2} + 3Na_2SO_4 + 2HC_2H_3O_2.$$

Aluminium Basic Acetate.—If a moderate excess of sodium or ammonium acetate be added to a dilute neutral or slightly acid solution of an aluminium salt and the liquid boiled, a white precipitate of basic aluminium acetate will be thrown down:

$$Al_2(SO_4)_3 + 6NaC_2H_3O_2 + 2H_2O$$
$$= Al_2(OH)_2(C_2H_3O_2)_4 + 3Na_2SO_4 + 2HC_2H_3O_2.$$

The precipitate is easily soluble in hydrochloric and sulphuric acids.

CHROMIUM (Cr). At. wt. 52.14; sp. gr. 6.8–7.3.

Chromium in the metallic state is rarely met with. It is sometimes alloyed with steel in the proportion of 0.5% to 0.75%, for the purpose of hardening the former.

It is readily soluble in chlorine or hydrochloric acid, and in sulphuric acid on warming.

Chromium occurs chiefly as oxide in combination with oxide of iron as chrome-ironstone FeO, Cr_2O_3.

Three oxides of chromium are known—Cr_2O_3, CrO_2, CrO_3. The monoxide has not been obtained in the anhydrous state, although its hydroxide is known.

Chromic oxide (Cr_2O_3) is green, the hydroxide a bluish green. The common salts of chromium are those of this oxide. They are all of a violet or green color, and many of them are soluble in water. Most of those not soluble in water are soluble in hydrochloric acid.

The oxygen salts of volatile acids are decomposed on ignition, leaving a residue of chromic oxide (Cr_2O_3) which is almost insoluble in acids.

Chromium Hydroxide.—Potassium and sodium hydroxides precipitate chromic salts, giving bluish-green precipitates of the hydroxide containing alkali (*a*). The precipitate is easily soluble in an excess of the reagent, yielding an emerald-green solution (*b*). From this solution on long boiling the hydroxide is reprecipitated (*c*). Addition of ammonium chloride effects the same result (*d*).

$$(a)\ Cr_2(SO_4)_3 + 6KOH = \underbrace{Cr_2(OH)_6} + 3K_2SO_4;$$

$$(b)\ \underbrace{Cr_2(OH)_6} + 2KOH = K_2Cr_2O_4 + 4H_2O;$$

$$(c)\ K_2Cr_2O_4 + 4H_2O = \underbrace{Cr_2(OH)_6} + 2KOH;$$

$$(d)\ K_2Cr_2O_4 + 2NH_4Cl + 4H_2O = \underbrace{Cr_2(OH)_6} + 2KCl + 2NH_4OH.$$

Ammonia and Ammonium Sulphide also give precipitates of chromic hydroxide which are slightly soluble in excess of ammonia. On boiling the precipitation is complete.

The Alkaline Carbonates give precipitates of basic carbonate, which dissolve with difficulty in an excess of the reagent.

Barium Carbonate precipitates chromium as a basic carbonate. The precipitation takes place in the cold, but requires long digestion to make it complete.

Sodium Phosphate in presence of sodium acetate precipitates neutral or slightly acid solutions as green chromic phosphate, $Cr_2(PO_4)_2$.

The presence of tartaric, citric, and oxalic acids, sugar, etc., interferes more or less with all of the precipitations of chromium that have been mentioned.

Oxidation to Chromic Acid.—The most characteristic reactions for chromium depend on its oxidation to chromate. The reaction is indicated by a change in color from green or violet to yellow or red. If any one of the precipitates already mentioned or any compound of chromium be fused (best in a platinum crucible) with four or five parts of a mixture of sodium carbonate and potassium chlorate in equal proportions, the chromium will be oxidized to chromate, Na_2CrO_4.

By dissolving the fused mass, which, if chromium is present is of a yellow color, in water, acidifying with acetic acid, and adding lead acetate, a yellow precipitate of lead chromate will be obtained:

$$Cr_2(OH)_6 + 2Na_2CO_3 + KClO_3$$
$$= 2Na_2CrO_4 + KCl + \overbrace{2CO_2} + \overbrace{3H_2O};$$
$$Na_2CrO_4 + Pb(C_2H_3O_2)_2 = \underbrace{PbCrO_4} + 2NaC_2H_3O_2.$$

A similar oxidation is effected by treating the solution of chromium hydroxide in potassium hydroxide ($K_2Cr_2O_4$) with bromine. In performing the operation the solution must be kept *alkaline* and the mixture warmed for some time and finally heated to boiling. The color changes from bluish green to yellow. If the solution be now acidified with acetic acid and a drop or two of lead acetate added, a yellow precipitate of lead chromate will be formed:

$$K_2Cr_2O_4 + 8KOH + 3Br_2$$
$$= 2K_2CrO_4 + 6KBr + 4H_2O.$$

Other oxidizing agents, as lead or sodium dioxides, or potassium permanganate, in alkaline solution, effect the same oxidation.

In a Bead of Borax or Sodium Metaphosphate in either the oxidizing or reducing flame, chromium compounds give an emerald-green color.

TITANIUM (Ti). At. wt. 48.1; sp. gr. 3.58.

Titanium is a comparatively rare metal, and is not found in the metallic state. It occurs as the dioxide, TiO_2, in several minerals, and is frequently met with in magnetic iron ores, and for this reason it is necessary to know something about its properties. The metal is easily soluble in acids, even in acetic.

It forms three oxides, TiO, Ti_2O_3, and TiO_2.

Salts of the last two oxides are known. TiO_2, besides acting as a basic oxide, also acts as a feeble acid.

Titanium dioxide after ignition is insoluble in acids, except in concentrated sulphuric and hydrofluoric. Fusion of the dioxide with potassium disulphate (the fusion should be continued for a considerable time, half an hour or more, at a low heat) yields a mass that is completely soluble in a large quantity of cold water (hot water must not be used, as metatitanic acid is precipitated from hot solutions).

Titanic oxide may also be readily brought into solution by fusing with potassium hydrogen fluoride and dissolving the fusion in dilute hydrochloric acid.

Solutions of titanium dioxide in hydrochloric or sulphuric acids are precipitated by the alkalies, the alkaline carbonates, ammonium sulphide, and barium carbonate *as titanic* acid, H_2TiO_3, a white flocculent precipitate insoluble in excess of the reagents. When thrown down from cold solution the precipitate is soluble in hydrochloric and sulphuric acids:

$$Ti(SO_4)_2 + 4KOH = \underbrace{H_2TiO_3} + 2K_2SO_4 + H_2O.$$

Sodium Phosphate precipitates solutions of titanium salts as a white precipitate of phosphate ($TiOHPO_4$). The precipitate forms even in solutions containing much hydrochloric acid.

Potassium Ferrocyanide added to acid solutions gives a bright reddish-yellow precipitate.

Sodium Thiosulphate precipitates nearly neutral solutions on boiling as titanic acid, H_2TiO_3 (separation from iron).

Precipitation on Boiling—Solutions of titanium in hydrochloric or sulphuric acids, not containing much free acid, on dilution with considerable water and boiling give a white precipitate of metatitanic acid insoluble in dilute acids. The solution best suited for this reaction is one in sulphuric acid containing only a slight excess of the acid. In order to insure complete precipitation the boiling must be continued for five or six hours, with renewal from time to time of the water lost by evaporation.

Hydrogen Peroxide gives with titanium solutions containing no fluoride an orange-yellow color. When iron is present a solution of the sulphate should be used.

Metallic Zinc or Tin added to acid solutions of titanic salts give a violet or blue color to the solution. The color often does not appear for some time, and the test is not very delicate.

SEPARATION.

The separation of the metals of the third group will be discussed later on in connection with those of the fourth group.

FOURTH GROUP.

IRON, ZINC, MANGANESE, COBALT, NICKEL.

THE metals of this group are distinguished from those of the fifth and sixth by the fact that they are not precipitated by hydrosulphuric acid (H_2S) from solutions acid with the mineral acids, and from those of the third group by their precipitation as sulphide and not hydroxide by ammonium sulphide.

The fact that they are precipitated as sulphides also distinguishes them from the metals of the first and second groups.

IRON (Fe). At. wt. 56; sp. gr. 7.8–8.2.

Iron is found in small quantities in the metallic state in some volcanic rocks and in meteorites. Compounds of iron are very widely distributed, and occur in enormous quantities particularly as oxide and sulphide.

Pure iron is a lustrous, grayish-white metal. It is hard, malleable, and ductile, fusing with difficulty, and is attracted by the magnet. In moist air or oxygen it is slowly oxidized to the hydrated sesquioxide (rust). When ignited in air or oxygen it forms the black magnetic oxide Fe_3O_4, or a mixture of this with ferric oxide, Fe_2O_3. Iron unites directly with the halogens, and with sulphur, carbon, boron, silicon, phosphorus, and arsenic. It also unites with many metals to form alloys.

Iron is readily soluble in dilute acids. In hydrochloric and dilute sulphuric acids it dissolves with evolution of hydrogen (*a*) in hot concentrated sulphuric acid, sulphurous anhydride is liberated (*b*) and ferric sulphate formed. With nitric acid the reaction varies according to temperature and strength of acid used. With cold dilute acid the products are ferrous nitrate and ammonium nitrate, and with hot moderately dilute acid ferric nitrate is formed (*c*, *d*).

(*a*) $Fe + H_2SO_4 = FeSO_4 + \overbrace{H_2}$;

(*b*) $2Fe + 6H_2SO_4 = Fe_2(SO_4)_3 + \overbrace{3SO_2} + 6H_2O$;

(*c*) $4Fe + 10HNO_3$

$= 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$;

(*d*) $2Fe + 8HNO_3 = Fe_2(NO_3)_6 + 2NO + 4H_2O$.

Three oxides of iron are known: ferrous oxide, FeO (also called protoxide); ferroso ferric oxide, Fe_3O_4 (magnetic or black oxide); and ferric oxide, Fe_2O_3 (peroxide, sesquioxide, or red oxide).

The ferrous and ferric oxides form two distinct series of salts having very different properties.

FERROUS COMPOUNDS.

Ferrous oxide is black, the hydroxide white. The latter absorbs oxygen very rapidly, and quickly changes in color, assuming first a greenish shade and finally becoming reddish brown. The oxide and hydroxide are both easily soluble in hydrochloric, nitric, and sulphuric acids. As already explained, ferrous salts are also formed by dissolving metallic iron in hydrochloric or dilute sulphuric or nitric acids (see equations *a* and *c*). Ferrous salts in the anhydrous state are white, in the hydrated green. The solutions unless concentrated have scarcely any color. These solutions absorb oxygen and change gradually to ferric salt with precipitation of basic compounds.

Oxidizing agents, as chlorine, bromine, or nitric id, quickly oxidize ferrous solutions to ferric:

$$6FeCl_2 + 8HNO_3$$
$$= 2Fe_2Cl_6 + Fe_2(NO_3)_6 + 2\overbrace{NO} + 4H_2O.$$

Ferrous salts of volatile oxygen acids are decomposed on ignition, leaving a residue of ferric oxide.

Ferrous Sulphide (*FeS*). — Hydrosulphuric acid in alkaline, and ammonium sulphide in neutral or alkaline, solutions of ferrous salts give black precipitates of ferrous sulphide, which are easily soluble in hydrochloric, nitric, and sulphuric acids. The presence of ammonium chloride aids the precipitation:

$$FeSO_4 + (NH_4)_2S = \underbrace{FeS} + (NH_4)_2SO_4;$$

$$\underbrace{FeS} + 2HCl = FeCl_2 + \overbrace{H_2S}.$$

Ferrous Hydroxide (*Fe*(*OH*)$_2$).—The hydroxides of potassium, sodium, and ammonium precipitate ferrous solutions as hydroxide, $Fe(OH)_2$. The presence of ammonium salts interferes with the precipitation by potassium or sodium hydroxide, and prevents the precipitation by ammonia. These alkaline solutions however quickly oxidize, and the iron then precipitates as ferroso-ferric or ferric hydroxide.

Ferrous Carbonate ($FeCO_3$).—The soluble carbonates give a white precipitate of ferrous carbonate, which rapidly oxidizes to the reddish-brown ferric hydroxide.

Barium carbonate does not precipitate ferrous salts in the cold, except solutions of the sulphate.

Ferrous Ferrocyanide.—Potassium ferrocyanide in neutral or slightly acid solutions produces a bluish-white precipitate of potassium ferrous ferrocyanide, $K_2Fe(FeC_6N_6)$, which on exposure to the air or by treatment with oxidizing agents changes to Prussian blue.

Ferrous Ferricyanide.—Potassium ferricyanide in neutral or slightly acid solutions produces a deep blue precipitate of ferrous ferricyanide, $Fe_3(FeC_6N_6)_2$ (Turnbull's blue):

$$3FeSO_4 + K_6(FeC_6N_6)_2 = \underbrace{Fe_3(FeC_6N_6)_2} + 3K_2SO_4.$$

Of all the tests for ferrous salts this is the most delicate and characteristic, the reaction taking place even in very dilute solutions.

FERRIC COMPOUNDS.

Ferric oxide is red or brownish red, and dissolves with more or less difficulty in acids even on heating. It is most easily gotten into solution by digesting with hot strong hydrochloric acid, or by fusion with potassium disulphate. Ferric hydroxide is reddish brown, and is easily soluble in acids. Ferric oxide and its hydrates are found very widely distributed, and in enormous quantities, and constitute the most important ores of iron.

Ferroso-ferric oxide, Fe_3O_4, is soluble in hot hydrochloric acid, the solution containing ferrous and ferric salt.

The normal ferric salts in the anhydrous state are white, the basic ones are red or yellow. Neutral ferric solutions are brownish yellow, the acid solutions yellow, and the color is visible even when much diluted. Salts of volatile oxygen acids are decomposed on ignition.

Ferrous Sulphide.—Hydrosulphuric acid added to acid solutions of ferric salts produces a white precipitate of sulphur, and the ferric compound is reduced to ferrous salt:

$$Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + \underset{\sim}{S}.$$

Ammonium sulphide in neutral or alkaline solution causes the same reduction (*a*), and the ferrous salt is then precipitated as sulphide (*b*).

$$(a)\ Fe_2Cl_6 + (NH_4)_2S = 2FeCl_2 + 2NH_4Cl + \underbrace{S};$$

$$(b)\ 2FeCl_2 + 2(NH_4)_2S = \underbrace{2FeS} + 4NH_4Cl.$$

The properties of this sulphide have already been described.

Ferric Hydroxide (*$Fe_2(OH)_6$*).—Potassium, sodium, and ammonium hydroxides give reddish-brown precipitates of the hydroxide, which are insoluble in an excess of the precipitant and in ammonium salts, but easily soluble in acids:

$$Fe_2Cl_6 + 6KOH = \underbrace{Fe_2(OH)_6} + 6KCl.$$

The *Soluble Carbonates* also give precipitates consisting principally of hydroxide, insoluble in excess of sodium and potassium carbonate.

Barium Carbonate even in cold solution precipitates the iron completely as hydroxide and basic salt.

Non-volatile organic acids or sugar interfere with or prevent the precipitation of ferric salts as hydroxide.

Ferric Acetate.—If to a neutral or slightly acid solution of a ferric salt an excess of sodium or ammonium acetate be added, the color changes to a reddish brown. .On diluting and boiling the solution a reddish-brown precipitate of basic acetate is thrown down. The precipitate is easily soluble in hydrochloric acid:

$$\begin{aligned} &Fe_2Cl_6 + 6NaC_2H_3O_2 + 2H_2O \\ &\quad = \underbrace{Fe_2(OH)_2(C_2H_3O_2)_4} + 6NaCl + 2HC_2H_3O_2. \end{aligned}$$

Ferric Phosphate.—Soluble phosphates in neutral or slightly acid solutions to which a slight excess of a soluble acetate has been added give yellowish-white precipitates of ferric phosphate, which are insoluble in acetic but soluble in the stronger acids:

$$\begin{aligned} &Fe_2Cl_6 + 2Na_2HPO_4 + 2NaC_2H_3O_2 \\ &\qquad\qquad = \underbrace{Fe_2(PO_4)_2} + 6NaCl + 2HC_2H_3O_2. \end{aligned}$$

Ferric Ferrocyanide.—Potassium ferrocyanide produces even in very dilute solutions a deep blue precipitate of ferric ferrocyanide, $Fe_4(FeC_6N_6)_3$ (Prussian blue).

The test is best made in a solution slightly acid with hydrochloric acid:

$$2Fe_2Cl_6 + 3K_4(FeC_6N_6) = \underbrace{Fe_4(FeC_6N_6)_3}_{} + 12KCl.$$

Potassium Ferricyanide produces no precipitate with a ferric salt, but changes the color of the solution to a dark brown (distinction from ferrous salts).

Ferric Thiocyanate. — Potassium thiocyanate (sulphocyanide) gives a deep red *color* of ferric thiocyanate, $Fe_2(CNS)_6$, even in excessively dilute solutions. The reagent should be added in moderate excess, and the solution be acid with hydrochloric acid. Certain acids, as acetic, tartaric, oxalic, phosphoric, hydrofluoric, arsenic, etc., interfere with the reaction, and when any one of them is present the hydrochloric acid must be added in large excess.

A similar color is produced by nitric acid if the acid be strong or the solution hot. By adding a little alcohol and warming, the color, if due to nitric acid, will disappear.

This test is the most characteristic and delicate for ferric salts. Ferrous salts give no color with the thiocyanate.

ZINC (Zn). At. wt. 65.4; sp. gr. 6.9–7.2.

Zinc is a bluish-white lustrous metal. At ordinary temperatures commercial zinc is brittle, but becomes malleable at temperatures between 100° C. and 150° C.; at 210° C. it becomes so brittle that it may be finely pulverized. It melts at 419° C., and boils at about 950° C., and may be easily distilled at a bright red heat, the vapors given off burning in the air with a bright white light and the formation of zinc oxide, ZnO. When exposed to the air zinc becomes gradually coated with a thin film of basic carbonate.

Zinc is found in considerable quantity, the principal ores being the carbonate, silicate, and sulphide.

Pure zinc is scarcely at all soluble in acids, but the presence of any impurity even in small amount causes it to dissolve easily. With dilute hydrochloric and sulphuric acids it evolves hydrogen (*a*). With very dilute nitric acid ammonium nitrate or nitrous oxide is formed (*b* and *c*), and in stronger acid nitric oxide (*d*).

It is also soluble in sodium or potassium hydroxides (*e*).

(*a*) $Zn + H_2SO_4 = ZnSO_4 + \overbrace{H_2}$;

(*b*) $4Zn + 10HNO_3$
$= 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$;

(*c*) $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + \overbrace{N_2O} + 5H_2O$;

(*d*) $3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 2NO + 4H_2O$;

(*e*) $Zn + 2KOH = K_2ZnO_2 + \overbrace{H_2}$.

Zinc forms one oxide, ZnO, white, and the hydroxide, $Zn(OH)_2$. Both are easily soluble in acids.

Zinc salts are colorless unless the acid be colored. Some are soluble in water, the rest in acids.

Zinc Sulphide (*ZnS*).—From neutral solutions of zinc salts, even those of the stronger acids, hydrosulphuric acid precipitates the greater part of the zinc as a white sulphide. From solutions of the acetate the precipitation is complete, even in presence of free acetic acid. For this reason if a moderate excess of sodium acetate be added to a neutral or slightly acid solution of a zinc salt in one of the stronger acids and H_2S be added, the
'e of the zinc will be precipitated as sulphide:

$$+ 2NaC_2H_3O_2$$
$$= \underbrace{ZnS} + 2NaCl + 2HC_2H_3O_2.$$

This reaction is particularly useful as a separation from manganese, which is not precipitated under these conditions.

Ammonium Sulphide in neutral or alkaline solutions produces the same white precipitate of sulphide. Presence of ammonium chloride aids the precipitation.

Zinc Sulphide is easily soluble in hydrochloric, nitric, and sulphuric acids, and insoluble in sodium, ammonium, or potassium hydroxides.

Zinc Hydroxide ($Zn(OH)_2$).—Sodium and potassium hydroxides produce white precipitates of zinc hydroxide, which are easily soluble in an excess of the precipitant. These alkaline solutions if concentrated are not precipitated on boiling, but when dilute the greater part of the zinc precipitates:

$$ZnCl_2 + 2KOH = \underbrace{Zn(OH)_2} + 2KCl\,;$$

$$\underbrace{ZnOH_2} + 2KOH = K_2ZnO_2 + 2H_2O.$$

Ammonium Hydroxide added to neutral or slightly acid solutions also precipitates the hydroxide, which is easily soluble in excess of the ammonia. Presence of ammonium salts or the presence of much free acid in the original solution (forming ammonium salt on addition of ammonia) interferes with or prevents the precipitation.

If the alkaline solution be boiled, the zinc partially precipitates if the solution be a concentrated one; if dilute the precipitation is complete.

Zinc Carbonate.—The soluble carbonates give white precipitates of basic carbonate, insoluble in excess of sodium or potassium carbonate, and soluble in excess of ammonium carbonate Presence of ammonium salts prevents these precipitations either wholly or partially according to the quantity present.

Barium Carbonate does not precipitate zinc salts from a cold solution, with the exception of the sulphate.

Zinc Cyanide.—Potassium cyanide throws down white zinc cyanide, which is easily soluble in excess of the reagent:

$$ZnCl_2 + 2KCy = \underbrace{ZnCy_2} + 2KCl;$$

$$\underbrace{ZnCy_2} + 2KCy = ZnCy_2,2KCy.$$

From this solution, if the excess of potassium cyanide is not great, the zinc may be precipitated as sulphide by the addition of sodium or potassium sulphide.

Hydrosulphuric acid and ammonium sulphide act slowly and imperfectly.

Color Test.—If to a solution of a zinc salt a few drops of cobalt nitrate (sufficient only to give a faint pink color) be added, the solution then made alkaline with sodium carbonate, boiled, filtered, and washed, and the precipitate ignited on a platinum capsule, a green mass will be obtained. The color shows more distinctly if the ignited precipitate be pulverized.

MANGANESE (Mn). At. wt. 55; sp. gr. 6.85–8.

Manganese is a whitish gray, lustrous metal, very hard and brittle. It is very difficultly fusible, its melting-point being about 1900° C.

It oxidizes very easily in the air, and decomposes water with evolution of hydrogen.

Manganese is easily soluble in all acids.

With copper it forms a valuable alloy resembling bronze, and alloyed with iron it forms spiegeleisen, or ferromanganese, used in the manufacture of steel.

Manganese forms a number of different oxides —MnO, Mn_3O_4, Mn_2O_3, MnO_2, and probably

MnO_3 and Mn_2O_7. The oxides MnO_3 and Mn_2O_7 are the anhydrides of manganic, H_2MnO_4, and permanganic acids, $H_2Mn_2O_8$. Manganic acid has not been separated, but many of its salts are known. The oxides MnO, Mn_3O_4, and Mn_2O_3 are basic oxides, and dissolve in hydrochloric or sulphuric acid, forming manganous or manganic salts. If the acid is hot the solutions contain only manganous salt. MnO_2 acts both as a basic and an acid oxide:

$$MnO + 2HCl = MnCl_2 + H_2O;$$
$$Mn_2O_3 + 6HCl \text{ (hot)} = 2MnCl_2 + \widetilde{Cl_2} + 3H_2O;$$
$$MnO_2 + 4HCl \text{ (hot)} = MnCl_2 + \widetilde{Cl_2} + 2H_2O;$$

$$2MnO_2 + 2H_2SO_4 \text{ (conc. hot)} = 2MnSO_4 + 2H_2O + \widetilde{O_2}.$$

The stable salts of manganese are those corresponding to manganous oxide, MnO. They are colorless or pink. Some are soluble in water, the rest in acids.

Manganous Sulphide (*MnS*). — Ammonium sulphide in neutral or alkaline solutions precipitates manganese as a flesh-colored sulphide. The precipitate is readily soluble in acids, even in acetic. On exposure to the air it turns brown, owing to oxidation. Presence of ammonium chloride helps the precipitation:

$$MnCl_2 + (NH_4)_2S = \underbrace{MnS} + 2NH_4Cl.$$

Manganous Hydroxide ($Mn(OH)_2$).—Potassium and sodium hydroxides give precipitates of manganous hydroxide which are white at first but quickly change to brown and finally to a dark-brown, almost black color, due to the precipitate oxidizing to a higher oxide, probably Mn_3O_4, xH_2O:

$$MnCl_2 + 2KOH = \underbrace{Mn(OH)_2} + 2KCl.$$

Ammonium Hydroxide added to neutral solutions causes a partial precipitation of the manganese as hydroxide, a portion remaining in solution as a double salt of manganese and ammonium. Solutions containing much free acid or ammonium salt are not precipitated by ammonia owing to the formation of this double salt:

$$2MnCl_2 + 2NH_4OH = \underbrace{Mn(OH)_2} + MnCl_2, 2NH_4Cl.$$

Manganous hydroxide is soluble in ammonium chloride, but after oxidation the precipitate is insoluble:

$$\underbrace{Mn(OH)_2}+4NH_4Cl=MnCl_2,2NH_4Cl+2NH_4OH.$$

The alkaline solution on standing absorbs oxygen, and a brown precipitate is thrown down.

Manganous hydroxide in presence of free alkali is oxidized to MnO_2,H_2O by bromine or hydrogen dioxide:

$$\underbrace{Mn(OH)_2}+2KOH+Br_2$$
$$=MnO_2,H_2O+2KBr+H_2O.$$

Bromine also precipitates solutions of manganous salts containing sodium acetate, as dioxide. Heating assists the reaction:

$$MnCl_2+4NaC_2H_3O_2+Br_2+3H_2O$$
$$=\underbrace{MnO_2,H_2O}+2NaCl+2NaBr+4HC_2H_3O_2.$$

Manganous Carbonate.—The soluble carbonates precipitate manganous salts as the normal carbonate or as a mixture of carbonate and hydroxide. The precipitate is insoluble in an excess of the precipitant.

Barium Carbonate produces no precipitate except in solution of the sulphate.

Sodium Manganate (Na_2MnO_4).—If any compound of manganese be fused in a platinum capsule with a mixture of sodium potassium carbonate and an oxidizing agent such as sodium nitrate, the fused mass on cooling will have a characteristic bluish-green color, due to the formation of sodium manganate:

$$3Mn(OH)_2 + Na_2CO_3 + 4NaNO_3 \\ = 3Na_2MnO_4 + \overbrace{CO_2} + \overbrace{4NO} + 3H_2O.$$

The same result may be obtained by fusing the substance in a bead of sodium potassium carbonate held in a loop of platinum wire, in the oxidizing flame of the blowpipe or Bunsen burner:

$$Mn(OH)_2+Na_2CO_3+O_2=Na_2MnO_4+\overbrace{CO_2}+H_2O.$$

Permanganic Acid ($H_2Mn_2O_8$).—If a few drops of a solution of a manganous salt, which must be free from chlorine or chloride, are boiled with a large excess of concentrated nitric acid, and then some lead dioxide* added and the solution diluted, the liquid will have a purple color from the permanganic acid formed in the reaction:

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*The lead dioxide should be tested in the same way to see if it contains any manganese, as the latter is sometimes found in it as an impurity.

$$2MnSO_4 + 2PbO_2 + 2HNO_3 \\ = H_2Mn_2O_8 + 2PbSO_4 + 2\overbrace{NO}.$$

Bead Test.—If any compound of manganese be fused in a borax or sodium metaphosphate bead in the oxidizing flame of the blowpipe or Bunsen burner, an amethyst-colored bead is obtained. In the reducing flame the color is destroyed.

COBALT (Co). At. wt. 58.9; sp. gr. 8.96.

Cobalt is steel-gray, lustrous, hard and malleable, and ductile at a red heat. It is slightly magnetic even at a full red heat. In the air at ordinary temperatures it does not oxidize. In hot dilute hydrochloric or sulphuric acid it dissolves with evolution of hydrogen, but the best solvent is dilute nitric acid. The solutions contain cobaltous salts.

Cobalt forms three distinct oxides, CoO, Co_3O_4, and Co_2O_3. With some few exceptions the stable salts of cobalt are those corresponding to cobaltous oxide, CoO.

The higher oxides are soluble in hydrochloric acid with evolution of chlorine and formation of cobaltous salts.

The cobaltous salts in solution or in the crystalline state are generally red or pink, and the anhydrous salts are mostly blue. A solution of cobaltous chloride on evaporating nearly to dryness changes to blue, but on addition of water the pink color is restored.

Cobaltous Sulphide (*CoS*). — Hydrosulphuric acid added to neutral cobaltous salts of the mineral acids causes a partial precipitation of the metal as sulphide. Presence of free strong acid prevents the precipitation. Neutral solution of the acetate is almost wholly precipitated, but presence of free acetic acid prevents the precipitation, or nearly so. If, however, an excess of an alkali acetate be present, then H_2S precipitates the cobalt completely, especially on heating, even in presence of free acetic acid.

Ammonium Sulphide added to neutral or alkaline solutions completely precipitates the metal as sulphide. Presence of ammonium chloride aids the reaction.

Cobalt sulphide is insoluble in alkalies, and nearly so in acetic acid. In hydrochloric acid it dissolves with difficulty, and when precipitated from hot solutions it is almost insoluble in that acid.

Nitric acid and aqua regia dissolve it on heating:

$$\mathrm{CoCl_2 + (NH_4)_2S = \underbrace{CoS} + 2NH_4Cl.}$$

Cobaltous Hydroxide $Co(OH)_2$.—Potassium and sodium hydroxides give at first a blue precipitate of basic salt, which on boiling is converted into the pale red hydroxide. The precipitate is insoluble in an excess of the dilute alkali, but soluble in acids and in ammonia and ammonium carbonate:

$$\mathrm{CoCl_2 + 2KOH = \underbrace{Co(OH)_2} + 2KCl.}$$

Ammonia in neutral solutions gives the same precipitate as sodium or potassium hydroxide, but it is easily soluble in an excess of ammonia, forming a brownish-yellow liquid. In acid solutions or those containing ammonium salts, ammonia gives no precipitate.

The precipitation of cobalt as hydroxide is interfered with or prevented by the presence of non-volatile organic acids or sugar.

Cobaltous Carbonate.—Sodium and potassium carbonates give precipitates of basic carbonate which are insoluble in excess of the reagent.

Barium Carbonate in the cold precipitates only a solution of the sulphate.

Cobaltous Cyanide.—Potassium cyanide produces a brownish-white precipitate of cobaltous cyanide which is very easily soluble in an excess of the precipitant, with formation of a double cyanide:

$$\mathrm{CoCl_2 + 2KCN = \underbrace{Co(CN)_2}_{} + 2KCl;}$$

$$\mathrm{\underbrace{Co\,(CN)_2}_{} + 4KCN = Co(CN)_2,4KCN.}$$

From this solution the cobaltous cyanide is reprecipitated on the addition of hydrochloric acid:

$$\mathrm{Co(CN)_2, 4KCN + 4HCl}$$
$$\mathrm{= \underbrace{Co(CN)_2}_{} + 4KCl + 4\overbrace{HCy}^{}.}$$

If to a solution of the double cyanide containing some excess of KCN a few drops of hydrochloric acid be added (so as to liberate some hydrocyanic acid) and the solution boiled, or better if it be mixed with some potassium hydroxide and chlorine or bromine added to the cold solution, the cobaltous double cyanide is changed to potassium cobalticyanide, $K_6Co_2(CN)_{12}$, from which solution acids do not reprecipitate the cobaltous cyanide.

The reaction with hydrochloric acid yielding free hydrocyanic is perhaps represented by the following equation:

$$2(Co(CN)_2, 4KCN) + 2HCN = K_6Co_2(CN)_{12} + 2KCN + \widetilde{H_2},$$

and with bromine or chlorine by this:

$$2(Co(CN)_2, 4KCN) + Br_2 = K_6Co_2(CN)_{12} + 2KBr.$$

Nickel forms no corresponding compound.

Potassium Cobaltic Nitrite.—If a moderate excess of potassium nitrite (it is well to add it in the solid form so as to avoid diluting the solution) be added to a cobaltous solution that has been made acid with acetic acid, the cobalt will be precipitated as a yellow precipitate of potassium cobaltic nitrite:

$$2Co(NO_3)_2 + 10KNO_2 + 4HNO_2 = K_6Co_2(NO_2)_{12} + 4KNO_3 + 2\widetilde{NO} + 2H_2O.$$

The more concentrated the solution the more quickly the reaction takes place. With dilute solutions the precipitation is very slow, often requiring as much as 24 hours or more before it is complete. Even with strong solutions the test should be allowed to stand for at least 12 hours. Nickel salts are not precipitated by potassium nitrite when cobalt and nickel only are present in the solution.

In the Borax Bead cobalt compounds give a beautiful deep blue color in either the oxidizing or reducing flame of the Bunsen burner or blowpipe. The test is exceedingly delicate and very characteristic.

NICKEL (Ni). At. wt. 58.7; sp. gr. 8.97–9.26.

Nickel is a lustrous white metal with a yellowish-gray tinge. It is hard, malleable, ductile and very tenacious, and slightly magnetic. It fuses with difficulty, and does not oxidize in the air at ordinary temperatures. On heating itdissolves slowly in hydrochloric and dilute sulphuric acids, but is easily soluble in dilute nitric acid. In concentrated nitric acid it is passive. In these solutions the nickel is in the form of nickelous salt.

Nickel is found in the metallic state in some meteorites. In its principal ores it exists in combination with arsenic or sulphur.

There are three oxides—NiO, Ni_3O_4, and Ni_2O_3. The ordinary salts of nickel are those corresponding to nickelous oxide, NiO. This oxide and its hydroxide, $Ni(OH)_2$, are green; both are readily soluble in hydrochloric, nitric, and sulphuric acids. The higher oxides dissolve in hydrochloric acid to nickelous salt, with evolution of chlorine.

In the anhydrous condition nickelous salts are usually of a yellow color, and in the hydrated state they are green.

Nickelous Sulphide (*NiS*).—Hydrosulphuric acid acts in the same manner with nickelous salts as with those of cobalt.

Ammonium Sulphide in neutral or alkaline solutions produces a black precipitate of nickelous sulphide, which is slightly soluble in ammonium sulphide, particularly in presence of much free ammonia.

This alkaline solution of the nickel sulphide is brown. By neutralizing the solution with acetic acid and warming the nickel sulphide is precipitated. The presence of ammonium chloride or acetate aids the precipitation of nickel as sulphide. Nickel sulphide is very slightly soluble in acetic acid, and dissolves with difficulty in dilute hydrochloric. It is easily soluble in nitric acid and in aqua regia on heating:

$$NiCl_2 + (NH_4)_2S = \underbrace{NiS} + 2NH_4Cl.$$

Nickelous Hydroxide (*$Ni(OH)_2$*).—Potassium and sodium hydroxides give a light green precipitate of nickelous hydroxide, which is insoluble in an excess of the precipitant:

$$NiCl_2 + 2KOH = \underbrace{Ni(OH)_2} + 2KCl.$$

Ammonia in neutral solution causes a slight turbidity, but on the further addition of the reagent this dissolves to a blue liquid containing a combination of nickelous salt and ammonia. In presence of ammonium salt or free acid ammonia gives no precipitate.

Nickelous Carbonate.—Sodium and potassium carbonates give precipitates of green basic carbonate of nickel, insoluble in excess of the reagent.

Barium Carbonate in the cold precipitates only solutions of the sulphate of nickel.

Nickelous Cyanide (*$NiCy_2$*).—Potassium cyanide produces a green precipitate of nickelous cyanide, which is readily soluble in an excess of the reagent. From this solution the nickelous cyanide is reprecipitated by acidifying the liquid with hydrochloric or sulphuric acids:

$$\mathrm{NiCl_2 + 2KCN = \underbrace{Ni(CN)_2} + 2KCl;}$$

$$\mathrm{\underbrace{Ni(CN)_2} + 2KCN = Ni(CN)_2, 2KCN;}$$

$$\mathrm{Ni(CN)_2, 2KCN + 2HCl = \underbrace{Ni(CN)_2} + 2KCl + 2\overbrace{HCN}.}$$

If the solution of the double cyanide be made strongly alkaline with potassium hydroxide and chlorine or bromine be added (care must be taken to keep the solution *alkaline*), the nickel will be precipitated as the black hydroxide, $\mathrm{Ni_2(OH)_6}$:

$$\mathrm{2(Ni(CN)_2, 2KCN) + 6KOH + Br_2 = \underbrace{Ni_2(OH)_6} + 2KBr + 8KCN.}$$

This reaction enables us to separate nickel from cobalt; the latter it will be remembered gives no precipitate under the same conditions, but changes to cobalticyanide, which remains in solution.

Bead Test.—When fused in the borax bead in the oxidizing flame nickel compounds give a reddish-brown color. With sodium metaphosphate the bead is yellow or reddish yellow in both flames.

SEPARATIONS — THIRD AND FOURTH GROUPS.

If we examine the reactions of the metals of the third and fourth groups with ammonia in presence of ammonium chloride, we find that those of the third group and ferric salts of the fourth are precipitated by this reagent as hydroxides, insoluble in an excess of the reagent. This would seem to offer an excellent method for separating these metals from the remaining ones of the fourth group, but it has been found in practice that these hydroxides if present in considerable quantity always carry down some of the other metals as well, so much so in fact that if the latter were present in small quantity only they might be completely precipitated.

By dissolving the precipitate in hydrochloric acid and reprecipitating with ammonia it is possible to remove them to some extent, but not entirely. When very exact results are not required, or when the hydroxides are present in small quantity, this separation may be used to advantage.

The reaction with barium carbonate in a solution of the chlorides affords one of the most accurate methods for separating the third-group and ferric salts from the fourth-group metals. The test should be made on a cold solution that is neutral or only slightly acid, and a moderate excess of the finely divided carbonate added (freshly precipitated barium carbonate acts most rapidly). The mixture must be allowed to stand for some time and until no more carbon dioxide is evolved. When this plan of separation is adopted the cobalt and nickel are generally separated first as sulphides.

The method of procedure is given in Scheme Number III.

The hydroxides of the third group and iron may be separated in various ways. If we make use of their different solubilities in excess of sodium or potassium hydroxide, we can separate the aluminium and chromium hydroxides, which are soluble, from that of iron (and titanium), which is insoluble.

The chromium and aluminium can then be separated from each other by oxidizing the chromium

[illegible]

THE SEPARATION AND [illegible]

[illegible]

If a solution containing [illegible]
acids and bases as well [illegible]
isolate the following [illegible]

1. PO₄ [illegible]
2. [illegible]
3. [illegible]
4. F
5. [illegible]

If the [illegible]
Note 1, Scheme [illegible]
phosphate, etc. [illegible]
made before proceeding [illegible]
portions of the solution are taken [illegible]
follows:

[illegible] slightly acidulate [illegible]
and dissolve [illegible]
acid, and add [illegible]
A yellow precipitate

the scheme with bromine in a solution of the cyanides is accurate and rapid. The precipitation of the cobalt with potassium nitrite, and of the nickel in the filtrate with potassium hydroxide, gives excellent results, but the test requires a long time before the precipitation is complete.

Zinc and manganese may be separated as given in the scheme, or, taking advantage of the difference in solubility of their sulphides in acetic acid, we can effect the same result by treating a solution of their acetates made acid with acetic acid, with H_2S; the zinc is thrown down as sulphide, and the manganese remains in the solution, from which, after filtering out the zinc sulphide, it may be precipitated as hydroxide with potassium hydroxide. Solution of salts of the stronger acids may be separated in the same way by adding a moderate excess of sodium acetate and acetic acid before precipitating with H_2S. The separation of the metals of the third and fourth groups is somewhat complicated in the presence of phosphates, silicates, organic matter, etc., and therefore requires some modification of the ordinary methods of analysis. In Scheme IV a method is given in which the presence of these acids is provided for.

NOTE 1.—If the solution to be analyzed is a filtrate from the separation of the fifth and sixth groups, the H_2S contained in it should be expelled by boiling. After this has been done, ferrous salts if present (determined by testing a few drops of the solution with potassium ferricyanide) are oxidized to ferric by the addition of a little concentrated nitric acid, and boiling.

A test for non-volatile organic matter must also be made at this point, unless it has already been tested for in the preliminary examination in the glass tube (see complete analysis). The test is made by evaporating a small quantity of the liquid, which should be made acid (best with sulphuric acid) if not so already, to dryness, and igniting gently. A black carbonaceous residue proves the presence of organic matter. In presence of much nitric acid or nitrate the blackening may be only transient, due to the carbon being quickly oxidized by the oxygen of the nitric acid or nitrate. In cases of this kind more or less deflagration will be noticed. Should organic matter be found, the main portion of the solution must be evaporated to dryness (best after addition of some concentrated nitric acid) and ignited at a temperature just sufficient to thoroughly carbon-

ize the organic matter present. No attempt should be made to burn off the carbon, as the high temperature necessary would make the oxides of iron, alumina, and chromium very insoluble. After the residue has been completely carbonized, add a small quantity of strong hydrochloric acid and a little water, and boil for some time, and filter. The filtrate is now ready to be tested with ammonia, ammonium sulphide, etc.

These preliminary operations completed, a small portion of the solution is taken and ammonium chloride and a slight excess of ammonia added. Note carefully whether the latter causes any precipitate, and if so what color it is, then add ammonium sulphide and see if it produces any further precipitate and of what color. (A light-colored precipitate would indicate the absence of metals yielding black sulphides, viz., iron, cobalt, and nickel.)

Should ammonia have produced a precipitate, and the original solution have an acid reaction (neutral solutions cannot contain phosphates), take another small portion of the liquid from which the H_2S has been expelled, and the iron oxidized, and add a moderate quantity of tartaric acid, then make alkaline with ammonia. If the latter still causes a precipitate it indicates the presence of phosphates, etc., of the second group, and the solution must be analyzed according to Scheme IV. The tartaric acid in this test is used to prevent the precipitation of iron, alumina, and chromium as hydroxides or phosphates.

If in the test last given ammonia produces no precipitate, the mixture is to be analyzed by Schemes II or III.

If in the first test ammonia gave no precipitate, metals of the third group and iron must be absent, and no further testing for them is necessary. Should ammonium sulphide also have produced no precipitate, the fourth group cannot be present, and the rest of the solution is tested at once for the second group.

Our preliminary tests completed, and the results indicating the absence of phosphates, etc., and the presence of third and fourth-group metals, we will return to the treatment of the main portion of our solution.

A moderate quantity of ammonium chloride is added to form a double salt with the manganese (and with magnesium if second-group metals are present), and to aid the precipitation of the fourth-group metals as sulphides. If the original solution is acid it may not be necessary to add any ammonium chloride, as sufficient may be formed when the solution is neutralized with ammonia. One will have to judge as to whether this is the case or no by noting the quantity of ammonia required to make the solution neutral.

After the addition of the ammonium chloride or its formation in the solution, enough ammonia is added to make the solution faintly alkaline. An excess is to be avoided, as it not only dissolves appreciable quantities of aluminium and chromium hydroxides, but also helps to carry nickel sulphide into solution.

The ammonium sulphide should be added until the solution after shaking smells distinctly of that reagent.

Thorough stirring or shaking, and heating the liquid gently for some time, aids the precipitation and causes the precipitate to collect in large particles that are more easily filtered. The precipitation is best made in a small flask that can be corked, and the mixture in it thoroughly shaken. The precipitate should be washed with water to which a few drops of ammonium sulphide have been added.

Note 2.—It is better to remove the precipitate

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from the filter-paper and treat it in a beaker or test-tube with the acid. It should be well shaken, so that every particle of the precipitate will come in contact with the solvent. In case the amount of the precipitate is small, it may be removed from the filter by making a hole in the point of the latter and washing the precipitate through with a little water.

If the treatment with acid leaves no black residue, cobalt and nickel cannot be present.

A small quantity of iron sulphide is sometimes left undissolved in the residue.

NOTE 3.—The test for cobalt with the borax bead is so delicate, even in the presence of large quantities of nickel, that no other test for it is generally required.

NOTE 4.—In the treatment with potassium cyanide care must be taken not to use too great an excess; a little more than enough to dissolve the precipitate first formed by the cyanide is sufficient. It must be remembered that cobalt and nickel cyanides dissolve in potassium cyanide very easily, and if there is any portion of the precipitate that does not go into solution readily it should be filtered out, as it is probably a little ferric hydroxide formed from a small amount of ferrous sulphide left undissolved by the hydrochloric acid in the first treatment of the sulphides. The solution must be kept decidedly *alkaline* with KOH, and a moderate quantity of bromine added.

NOTE 5.—After the solution has been evaporated to expel the excess of acid, it must be diluted with very little water, so as to keep it concentrated, and the solution of potassium hydroxide should be strong, and added in considerable excess in order to insure solution of the zinc. A few drops of pure bromine (not bromine water) are then added if the color indicates chromium, and the solution gently heated for a few minutes to make sure of oxidizing the latter; the liquid is then boiled for a short time and filtered. In making this separation care must be taken to keep the mixture strongly alkaline.

NOTE 6.—This precipitate may be tested for manganese by fusing it in a platinum capsule with a mixture of sodium potassium carbonate and sodium nitrate, when the green manganate will be formed.

NOTE 7.—The state of oxidation of the iron is of course not shown by this test. In order to determine it, the original solution must be tested before any oxidizing or reducing agents have been added, with potassium ferricyanide for ferrous salts and the thiocyanate for ferric.

Note 8.—Titanium is so seldom met with except in the analysis of some iron ores and furnace products, that its presence is rarely considered in an ordinary analysis. When required to test for titanium it is better to fuse some of the original material with potassium disulphate, dissolve the fusion in cold water, and test with hydrogen dioxide, or metallic zinc, or any other characteristic test.

Note 9.—If this solution be saturated with H_2S, aluminium if present would be precipitated as hydroxide. It can, however, be easily distinguished from zinc sulphide by adding some more potassium hydroxide, in which it is readily soluble, while the zinc sulphide is insoluble.

Note 10.—An excess of ammonia must not be added. Heating the solution helps the precipitation of the aluminium hydroxide. The precipitate is insoluble in ammonium chloride (distinction from zinc hydroxide).

Since alumina and silica are common impurities in sodium or potassium hydroxides, it is always well to take a quantity of the alkali equal to that *used in* the test for alumina, and treat it with hydrochloric acid and ammonia in precisely the same way, and if any precipitate is obtained compare it with that from the regular test. If much less, it is safe to conclude that the substance under examination contains alumina.

NOTE 11.—Only a drop or two of the lead acetate should be added, so as to avoid the precipitation of lead chloride or bromide, as any considerable quantities of these white precipitates might hide small amounts of the yellow chromate.

SCHEME IV.

THE SEPARATION AND DETECTION OF AL, CR, FE, CO, NI, MN, ZN, BA, CA SR, AND MG IN THE PRESENCE OF PHOSPHORIC, OXALIC, BORIC, SILICIC, OR HYDROFLUORIC ACID.

If a solution containing the above-mentioned acids and bases is made alkaline with ammonium hydrate the following is likely to occur:

H_3PO_4	ppts.	Al	Cr	Fe(ic)	Co	Ni	Mn	Zn	Ba	Sr	Ca	Mg
H_3BO_3	"	"	"	"	"	"	"	"	"	"	"	"
H_2SiO_3	"	"	"	"	"	"	"	"	"	"	"	"
HF	"	"	"	"	"	"	"	"	"	"	"	"
$H_2C_2O_4$	"	chiefly							"	"	"	

If the test with tartaric acid and ammonia (*see* Note 1, Scheme II) has indicated the presence of phosphate, etc., a few preliminary tests should be made before proceeding further. Several small portions of the solution are taken and tested as follows:

I. Make slightly alkaline with ammonia, filter out precipitate and dissolve it in a small quantity of dilute nitric acid, and add an excess of ammonium molybdate. A yellow precipitate proves the

CO_3 M

Ppt. 29 { $Al_2(PO_4)_2$

Sol. 29 { Na_2CrO_4, KCl, $NaC_2H_3O_2$, $HC_2H_3O_2$, Na_2HPO_4

KCy

1° + Na_2HPO_4

{ $Al_2(OH$, $Cr_2(OH$, H_2TiO_3, $Fe_2(OH$, $BaCO_3$ } 2° + $Pb(C_2H_3O_2)_2$

Ppt. 30 { $PbCrO_4$

Sol. 30 { $Al_2(C_2H_3O_2)_6$, $NaC_2H_3O_2$, KCl, $HC_2H_3O_2$, $Pb(C_2H_3O_2)_2$

3 { $Fe_2(CyS)_6$

l_6 (violet color)

√

{ $ZnCl_2$, $MnCl_2$, $BaCl_2$, NaCl

To follow Scheme III.

presence of phosphoric acid. (Arsenic acid, which acts like phosphoric, will have been removed with the fifth and sixth group metals as sulphide.)

II. Oxalates are seldom met with in an analysis. They may be detected by heating the solution (the more concentrated the better) with some manganese dioxide (free from carbonate) and a little dilute sulphuric acid. If present, there will be an effervescence and evolution of carbon dioxide (CO_2), which may be recognized by its action on lime-water (*see* Carbonic Acid).

III. Silicic acid when present is generally removed before beginning the tests for the metals by evaporating an acid solution to dryness and taking up the residue with acid and water (*see* Silicic Acid).

The same test may be applied here if necessary.

Borates and fluorides are usually held in solution (or sufficiently so) by the ammonium chloride present, so that they do not interfere to any great extent, and no modification of the method of analysis is required.

We are now ready to proceed with the separation, supposing the presence of phosphates, etc., to have been shown by the tests just made.

Boil out H_2S, if present. Add a few drops of HNO_3 and boil (Note 1). If $H_2C_2O_4$ or organic matter is present, evaporate to dryness and ignite gently. If these are not present, but silicic acid is, then acidify with HCl and evaporate to dryness, but do not ignite (Note 2). Treat the residue with HCl (conc.), dilute with H_2O, and boil; it dissolves wholly or leaves a white residue of SiO_2. Filter. If neither oxalic nor silicic acids are present the solution after boiling with nitric acid to oxidize the iron is treated according to filtrate 1°.

<table>
<tr><td>RESIDUE 1°.
SiO_2.</td><td colspan="3">FILTRATE 1.°
Nearly neutralize with NH_4OH, then add a moderate excess of $NH_4C_2H_3O_2$ and a little $HC_2H_3O_2$, dilute largely, boil for about 5 min., and filter. Wash the ppt. with boiling water. (Note 3.)</td></tr>
<tr><td colspan="2">PPT. 2°.
Fe, Al, and Cr as phosphates and basic acetates.
Dry and mix with $Na_2CO_3 + KClO_3$, and fuse in platinum capsule. Dissolve the fusion in boiling water, and filter. (Note 4.)</td><td colspan="2">FILTRATE 2°.
Metals of the 1°, 2°, and 4° Groups, except iron.
Analyze in the same way as any ordinary mixture of the first four groups.</td></tr>
<tr><td rowspan="2">RESIDUE 3°.
$Fe_2O_3, Al_2O_3, Fe_2(PO_4)_2$, and $Al_2(PO_4)_2$.</td><td colspan="3">SOLUTION 3°.
Na_2CrO_4, $Na_2Al_2O_4$, etc. (Divide in 2 parts.)</td></tr>
<tr><td colspan="2">1° acidify with $HC_2H_3O_2$ (if any precipitate forms, it shows $AlPO_4$); filter, and to the filtrate add $Pb(C_2H_3O_2)_2$, a yellow ppt. = $PbCrO_4$; proves Cr.</td><td>2° acidify with HCl; then add $(NH_4)_2CO_3$, and boil. A white, flocculent precipitate proves Al.</td></tr>
</table>

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then be added. If iron or aluminium salts are present, a precipitate of their phosphates may then be thrown down. If sufficient iron is present to precipitate all the phosphoric acid, the solution, after the addition of the ammonium acetate, will have a red color, due to ferric acetate. If the solution, however, remains colorless, ferric chloride must be added, drop at a time, until the red color appears or until a few drops of the liquid give a red precipitate with ammonia. Any large excess of iron is to be avoided, but enough to give a reddish tinge to the liquid is necessary to insure complete precipitation of the phosphoric acid.

The ferric acetate is precipitated on boiling the dilute solution as a basic acetate, and any ferric phosphate that it may have been held in solution is thrown down at the same time. A small amount of free acetic acid is necessary in the reaction to prevent any zinc or manganese precipitating. The solution should not be boiled more than four or five minutes, and it must be quite dilute.

The filtration should be carried on rapidly, the liquid being kept hot, and the precipitate washed with boiling water.

NOTE 4.—Although aluminium phosphate is not completely decomposed by fusion with sodium carbonate, still sufficient of it goes into solution to give a satisfactory test for aluminium.

Another method that could be used would be to treat the precipitate with potassium hydroxide. The aluminium and chromium basic acetates and phosphates are soluble in this reagent, and go into solution. The chromium is then oxidized in the alkaline solution with bromine, and the chromium determined in one portion by acidifying with acetic acid, filtering if necessary, and adding lead acetate. The alumina is determined in the other part by acidifying with hydrochloric acid and then making alkaline with ammonia.

NEW YORK CITY

METALS OF THE FIFTH GROUP.

The common metals of this group are: Silver (Ag), Lead (Pb), Mercury (Hg), Bismuth (Bi), Copper (Cu), and Cadmium (Cd).

The chief characteristics of the group are the precipitation of the metals by H_2S from acid solutions, and the insolubility of these precipitates in alkaline sulphides (note exceptions to latter under mercury and copper).

H_2S or alkaline sulphides also precipitate neutral or alkaline solutions in the same way.

The group is subdivided into two divisions, the first comprising the metals yielding chlorides insoluble in dilute hydrochloric or nitric acids, viz., silver, lead, and mercurous salts. Lead is often found in both divisions, owing to the fact that its chloride is not very insoluble in water, and even more soluble in solutions of certain salts.

We will now proceed to a study of the individual metals of the group, and when that has been completed the separation of the group from the other groups, and the detection of its different metals, will be explained.

SILVER (Ag). At. wt. 108; sp. gr. 10.53.

A white, lustrous metal, very malleable, fuses at 954° C. It is not oxidized by water or air at any temperature; is easily attacked by Cl, Br, or I, and is quickly tarnished by H_2S or sulphides.

The proper solvent is nitric acid, in which it is readily soluble. It is also soluble in hot strong sulphuric acid.

$$6Ag + 8HNO_3 = 6AgNO_3 + 2NO + 4H_2O;$$

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + \overset{\frown}{SO_2} + 2H_2O.$$

Silver Chloride (*AgCl*).—Hydrochloric acid or soluble chlorides when added to solutions of silver salts give a white curdy precipitate of silver chloride (*a*) which blackens on exposure to light. The precipitate is insoluble in dilute hydrochloric and nitric acids, but is somewhat soluble in the strong acids. It is easily soluble in ammonia (*b*), from which solution it reprecipitates on acidifying with nitric acid (*c*). Also soluble in potassium cyanide as double cyanide (*d*), and in sodium thiosulphate (hyposulphite) ($Na_2S_2O_3$) (*e*). Soluble to a considerable extent in concentrated solutions of chlorides of the alkalies. The double cyanide solution is largely used in electroplating, and the reaction with thiosulphate is made constant use of in photography, also in the extraction of silver from its ores.

(*a*) $AgNO_3 + HCl = \underbrace{AgCl}_{} + HNO_3;$

(*b*) $\underbrace{2AgCl}_{} + 3NH_4OH = 2AgCl,3NH_3 + 3H_2O;$

(*c*) $2AgCl,3NH_3 + 3HNO_3 = \underbrace{2AgCl}_{} + 3NH_4NO_3;$

(*d*) $AgCl + 2KCy = AgCy,KCy + KCl;$

(*e*) $2AgCl + 3Na_2S_2O_3$
$= Ag_2S_2O_3,2Na_2S_2O_3 + 2NaCl.$

Silver chloride may be reduced to metal by adding to it a piece of zinc and a little dilute acid, as sulphuric:

$$2AgCl + Zn = \underbrace{Ag}_{} + ZnCl_2.$$

Fusion of the chloride with sodium carbonate effects the same result.

Silver Bromide ($AgBr$).—Soluble bromides precipitate silver salts, giving a yellowish-white precipitate of bromide, insoluble in dilute nitric acid and less easily soluble in ammonia than the chloride. Soluble in potassium cyanide and thiosulphate, the same as the chloride. Decomposed by concentrated hydrochloric acid, with formation of $AgCl$.

Silver Iodide (AgI).—Soluble iodides give a yellow precipitate of silver iodide, soluble in excess of the reagent, forming a double iodide, and in potassium cyanide and thiosulphate. It is almost insoluble in ammonia. Insoluble in dilute acids.

Silver Cyanide ($AgCy$).—HCy or soluble cyanides give white precipitates of silver cyanide, easily soluble in excess of reagent. Insoluble in dilute nitric acid, and decomposed by the boiling concentrated acid. Soluble in ammonia and thiosulphate. Decomposed on ignition into metallic silver, cyanogen gas, and paracyanogen.

Silver Sulphide (Ag_2S).—H_2S or soluble sulphides precipitate silver salts, giving a black precipitate of silver sulphide, insoluble in cold dilute acids, in alkaline sulphides, and in potassium cyanide. Easily soluble in boiling dilute nitric acid, with separation of sulphur:

$$2AgNO_3 + H_2S = \underbrace{Ag_2S} + 2HNO_3;$$

$$3\underbrace{Ag_2S} + 8HNO_3 = 6AgNO_3 + 3S + 2\overbrace{NO} + 4H_2O.$$

Silver Oxide (Ag_2O).—Sodium or potassium hydrates precipitate solutions of silver salts, yielding brown silver oxide, insoluble in excess of the reagent:

$$2AgNO_3 + 2KOH = Ag_2O + 2KNO_3 + H_2O.$$

Ammonium hydrate gives the same precipitate in neutral solutions, easily soluble in excess of ammonia ($Ag_2O,2NH_3$).

Silver oxide is decomposed by heat into metallic silver and oxygen.

Silver can easily be obtained in the metallic state from its solutions by the addition of one of the more electropositive metals, as Cu, Zn, Hg, Fe etc., also by many reducing agents, as $FeSO_4$, SO_2, etc.

LEAD (Pb). At. wt. 207; sp. gr. 11.4.

Lead is a soft, malleable metal, of a gray color, fusing at 335° C. It is insoluble in dilute sulphuric and hydrochloric acids, but dissolves easily in dilute nitric acid:

$$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2\widetilde{NO} + 4H_2O.$$

Water containing air acts on lead forming a hydrate, which soon changes to a basic carbonate. This action is increased by the presence of nitrogenous organic matter, also by nitrates and nitrites.

Lead forms several oxides (PbO, Pb_3O_4, PbO_2, etc.). On ignition the higher oxides are all reduced to PbO, which is the only oxide forming stable salts.

Lead oxide (PbO) is a yellow substance soluble in nitric and acetic acids, also in sodium and potassium hydrates.

All the stable salts of lead are those of this oxide.

Triplumbic tetroxide, or red lead (Pb_3O_4), is, as the name implies, of a red or scarlet color. It is largely used as a pigment.

With nitric acid it gives lead nitrate, $Pb(NO_3)_2$, soluble, and leaves a brown residue of lead dioxide (PbO_2). Hydrochloric acid slowly dissolves it, with evolution of chlorine.

Reducing agents, as oxalic or tartaric acids, sugar, or alcohol, cause it to dissolve completely in nitric acid.

Lead dioxide, often called puce or peroxide, is of a brown color. It is insoluble in nitric acid except when reducing agents are present. With hydrochloric acid it yields lead chloride and chlorine.

Lead Chloride ($PbCl_2$).—In solutions of lead salts, not too dilute, hydrochloric acid or soluble chlorides give a white precipitate of lead chloride, only slightly soluble in cold water, but soluble in hot. In dilute hydrochloric acid it is more insoluble than in water. In strong hydrochloric or nitric acid it is much more soluble than in water:

$$Pb(NO_3)_2 + 2HCl = \underbrace{PbCl_2} + 2HNO_3.$$

If ammonia be added to lead chloride it changes it to a basic chloride, $PbCl_2,3PbO,4H_2O$, which is very insoluble in water.

Lead Bromide ($PbBr_2$).—Soluble bromides precipitate lead salts as bromide, white, solubility in water about the same as the chloride.

Lead Iodide (*PbI_2*).—Soluble iodides precipitate lead iodide, yellow, more insoluble in water than the chloride or bromide. Soluble in excess of the reagent, forming double iodides (as KI,PbI_2 or $4KI,PbI_2$).

Lead Sulphide, PbS.—H_2S or soluble sulphides give with lead salts a black precipitate of PbS (*a*). In presence of much hydrochloric acid the precipitate is sometimes red, owing to the formation of a compound of lead chloride and sulphide (as $PbCl_2,2PbS$); on diluting the solution with water and adding an excess of H_2S, the red precipitate is converted into the black sulphide.

Lead sulphide is easily soluble in hot dilute nitric acid, yielding lead nitrate (*b*). With hot concentrated acid it gives lead sulphate (*c*).

$$(a)\quad Pb(NO_3)_2 + H_2S = \underbrace{PbS} + 2HNO_3;$$

$$(b)\quad 3PbS+8HNO_3 = 3Pb(NO_3)_2+2\overbrace{NO}+3\underbrace{S}+4H_2O$$

$$(c)\quad 3PbS+8HNO_3 = \underbrace{3PbSO_4} + 8NO + 4H_2O.$$

Lead Sulphate (*$PbSO_4$*).—Sulphuric acid and soluble sulphates precipitate lead salts as sulphate (*a*), white, insoluble in water, and in dilute acids, particularly dilute sulphuric.

Concentrated hydrochloric dissolves it as lead chloride. It is soluble in boiling ammonium acetate and in the fixed alkalies. Also soluble in warm (68° C.) sodium thiosulphate (*b*) (distinction from barium sulphate). Presence of much free nitric acid interferes with the precipitation of lead as sulphate.

$$(a)\ Pb(NO_3)_2+H_2SO_4=\underbrace{PbSO_4}+2HNO_3;$$

$$(b)\ \underbrace{PbSO_4}+3Na_2S_2O_3$$
$$=2Na_2S_2O_3,PbS_2O_3+Na_2SO_4.$$

Lead Hydroxide ($Pb(OH)_2$).—Sodium or potassium hydrates precipitate lead solutions as hydroxide, white, soluble in excess of the reagent:

$$Pb(NO_3)_2+2KOH=\underbrace{Pb(OH)_2}+2KNO_3;$$

$$\underbrace{Pb(OH)_2}+2KOH=K_2PbO_2+2H_2O.$$

Ammonia gives precipitates of basic salts, insoluble in excess of ammonia.

With solutions of the acetate not too concentrated, ammonia gives no precipitate owing to the formation of a soluble tribasic acetate ($Pb_3O_2(C_2H_3O_2)_2$).

Lead Carbonate. — Soluble carbonates give white precipitates of basic lead carbonates, variable in composition.

Lead Chromate ($PbCrO_4$).—Solutions of lead salts are precipitated by soluble chromates, giving a precipitate of lead chromate, yellow, soluble in sodium or potassium hydrates, insoluble in dilute nitric and acetic acids:

$$Pb(NO_3)_2 + K_2CrO_4 = \underbrace{PbCrO_4} + 2KNO_3.$$

In addition to the compounds spoken of, the phosphate, oxalate, cyanide (there is no double cyanide), and sulphite are insoluble in water.

Lead salts are easily reduced to the metallic state by the more electropositive metals, such as zinc, iron, or magnesium.

If any lead compound is heated on charcoal in the reducing flame of the blowpipe, the lead is reduced to the metallic state (*a*), and a portion volatilizes and forms a coating of lead oxide on the coal. This coating is dark yellow when hot, light yellow on cooling.

The addition of sodium carbonate to the substance before the fusion on charcoal assists the reaction very materially (*b*).

(*a*) $PbSO_4 + C = Pb + \widetilde{CO_2} + \widetilde{SO_2}$.

(*b*) $2PbSO_4 + 2Na_2CO_3 + 5C = 2Pb + 2Na_2S + 7\widetilde{CO_2}$.

If, instead of making the fusion on charcoal, the mixture of Na_2CO_3 with the lead compound be fused in a porcelain crucible, the reaction is different, the lead being obtained as oxide :

$$PbSO_4 + Na_2CO_3 = PbO + Na_2SO_4 + \widetilde{CO_2}.$$

MERCURY (Hg). At. wt. 200; sp. gr. 13.59.

A white lustrous metal; liquid at temperatures between −40° C. and 360° C.

At the latter temperature it boils and volatilizes. It is slightly volatile at ordinary temperatures. When in a very finely divided state the metal appears as a gray or black pulverulent powder, without metallic lustre. It is not oxidized by the air. The best solvent is nitric acid.

It dissolves easily in dilute acid on heating, or in the cold if lower oxides of nitrogen are present. With cold dilute acid the product is mercurous nitrate (*a*), with hot acid in excess mercuric nitrate (*b*).

It is also soluble in strong sulphuric acid on heating (*c*) and in chlorine.

(*a*) $6Hg + 8HNO_3 = 3Hg_2(NO_3)_2 + 2\widetilde{NO} + 4H_2O;$

(*b*) $3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 2\widetilde{NO} + 4H_2O;$

(*c*) $Hg + 2H_2SO_4 = HgSO_4 + \widetilde{SO_2} + 2H_2O.$

Hydrochloric acid does not dissolve it.

A very characteristic property of mercury is its power of forming amalgams with many other metals. This is made use of on a very large scale for the extraction of gold and silver from their ores.

To a few drops of mercury in a watch-glass add a little finely divided lead or zinc, and notice that the lead or zinc dissolves in the mercury, and that the latter becomes pasty. By igniting the amalgam gently the mercury volatilizes and the metal with which it was combined is left as a residue.

Mercury forms two well-defined oxides, mercurous oxide (Hg_2O), black, and mercuric oxide (HgO), red, and two corresponding series of salts.

Mercurous Salts.

With the exception of the nitrate ($Hg_2(NO_3)_2$), the mercurous salts are insoluble or difficultly so in water.

The oxygen salts are volatile on ignition, undergoing decomposition at the same time. The chloride and bromide volatilize unaltered.

Hg_2Cl_2.—Hydrochloric acid or soluble chlorides give with mercurous salts a white precipitate of Hg_2Cl_2 (calomel).

This precipitate is insoluble in cold hydrochloric acid, but on boiling is slowly changed to mercuric chloride ($HgCl_2$) and metallic mercury (Hg).

Chlorine or nitric acid quickly change it to mercuric salt, soluble in water. KOH or NaOH convert it into mercurous oxide (Hg_2O), black. NH_4OH also turns it black, but the product is a mixture of a mercuric ammonium compound and metallic mercury, insoluble in excess of ammonia (distinction from silver):

$$Hg_2(NO_3)_2 + 2HCl = \underbrace{Hg_2Cl_2} + 2HNO_3;$$

$$\underbrace{Hg_2Cl_2}_{\text{white}} + 2NH_4OH$$

$$= \underbrace{NH_2HgCl + Hg}_{\text{black}} + NH_4Cl + 2H_2O.$$

HBr or soluble bromides precipitate mercurous solutions, giving a precipitate of mercurous bromide (Hg_2Br_2), yellowish white; insoluble in dilute HNO_3.

Soluble iodides give a greenish-yellow precipitate of Hg_2I_2, which is slowly decomposed by excess of the reagent to $HgI_2,2KI + Hg$.

Sulphides.—H_2S or soluble sulphides precipitate from mercurous solutions a mixture of $HgS + Hg$ (black). The metallic mercury may be dissolved out by boiling with dilute HNO_3; the HgS remains insoluble.

Oxide.—KOH or NaOH gives black precipitates of mercurous oxide (Hg_2O) when added to mercurous solutions. The precipitate is insoluble in excess of the alkali.

NH_4OH also gives a black precipitate of mercuric ammonium salt and metallic mercury, insoluble in excess of ammonia.

Reducing agents, as $SnCl_2$, $FeSO_4$, etc., quickly reduce mercurous solutions, giving a precipitate of metallic mercury (gray or black).

SECOND DIVISION—NOT PRECIPITATED BY HYDROCHLORIC ACID.

Mercuric Salts.

With the exception of the chloride, most of the mercuric salts require for their solution in water the presence of some free acid; otherwise they decompose, giving a precipitate of basic salt.

Like the mercurous salts they are all volatile on ignition.

HgS.—If H_2S or ammonium sulphide be added gradually to mercuric solutions, a white precipitate is first formed, which changes, on further addition of the reagent, to yellow, then brown, and finally, when the reagent is in excess, to a black precipitate.

The lighter-colored precipitates consist of combinations of the mercuric salt with HgS, in varying proportions (*a*). The final, black, precipitate is mercuric sulphide (*b*).

$$(a)\ 3HgCl_2 + 2H_2S = \underbrace{HgCl_2,2HgS} + 2HCl;$$

$$(b)\ HgCl_2 + H_2S \quad = \underbrace{HgS} + 2HCl.$$

The precipitate is insoluble in nitric acid, even on boiling (a distinction from all other sulphides of the group). On long boiling with strong nitric acid it is changed in color from black to white, the change being due to the nitric acid displacing some of the sulphur of the sulphide, and forming a compound similar in composition to the one given by H_2S when not added in excess (*a*) ($Hg(NO_3)_2,2HgS$). This, like HgS, is insoluble in nitric acid, but is soluble in chlorine.

HgS is readily soluble in aqua regia (*i.e.*, chlorine). It is slightly soluble in boiling dilute hydrochloric, much more so in the concentrated acid. Sodium or potassium sulphides, particularly in presence of free alkali, dissolve it, with the formation of double salts.

Oxide.—KOH or NaOH added to neutral or slightly acid solutions of mercuric salts give at first a reddish-brown precipitate of basic salt, which changes on further addition of the alkali to yellow mercuric oxide (*a*). The precipitate is insoluble in excess.

In presence of ammonia salts the precipitate is white (*b*)

$$(a)\ HgCl_2 + 2KOH = \underbrace{HgO}_{\text{yellow}} + 2KCl + H_2O;$$

$$(b)\ HgCl_2,NH_4Cl + 2KOH$$
$$= \underbrace{(NH_2Hg)Cl} + 2KCl + 2H_2O.$$

Ammonia produces similar precipitates to the one given in (*b*) unless the solution contains much free acid, in which case no precipitate is formed:

$$HgCl_2 + 2NH_4OH = \underbrace{NH_2HgCl} + NH_4Cl + 2H_2O.$$

Reduction to Metal.—Stannous chloride when added to mercuric solutions gives at first a white precipitate of mercurous chloride, which on further addition of the reagent changes to metallic mercury, gray or black:

$$2HgCl_2 + SnCl_2 = \underbrace{Hg_2Cl_2}_{\text{white}} + SnCl_4;$$

$$\underbrace{Hg_2Cl_2} + SnCl_2 = \underbrace{2Hg}_{\text{black}} + SnCl_4.$$

Other reducing agents, such as $FeSO_4$, SO_2, $Na_2S_2O_3$, etc., also reduce either mercurous or mercuric solutions to the metallic state.

If a piece of bright, clean copper be placed in a neutral or slightly acid solution containing either mercurous or mercuric salt, the copper will soon be covered with a gray coating of mercury. If this deposit be gently rubbed with a piece of filter-paper or cloth, it becomes bright and lustrous like polished silver. On gently warming, the coating volatilizes and the color of the copper reappears.

If any *dry* salt of mercury, either mercurous or mercuric, be mixed with dry sodium carbonate and heated in a glass tube closed at one end, metallic mercury will be volatilized and condense in the cold upper portions of the tube as a metallic mirror.

BISMUTH (Bi). At. wt. 210; sp. gr. 9.9.

Bismuth is a hard, brittle metal, of a white color with a reddish lustre. Fuses at 264° C. It is very slightly oxidized by the air at ordinary temperatures, but very rapidly at a red heat.

It is almost insoluble in hydrochloric acid; boiling sulphuric converts it into sulphate, but its best solvent is nitric acid:

$$2Bi + 8HNO_3 = 2Bi(NO_3)_3 + 2\overset{\frown\frown}{NO} + 4H_2O.$$

There are several different oxides of bismuth, but the only one forming stable salts is the oxide Bi_2O_3.

Precipitation by Water.—Bismuth salts require for their solution in water the presence of some free acid, otherwise they decompose into basic salts which precipitate. This action is very characteristic and important, and is made much use of in analysis.

If to a solution of bismuth chloride an excess of water be added, the greater part of the bismuth is precipitated as an oxychloride (*a*). With solution of the nitrate, the precipitate is variable, depending on the quantity of water added (*b* and *c*).

In this reaction a portion of the bismuth is always held in solution by the nitric acid liberated. With bismuth chloride the precipitation is complete if excess of free acid has been removed by evaporation or neutralization before making the test. In solutions of the nitrate the delicacy of the reaction is greatly increased if to the solution, which should be only slightly acid and concentrated, a solution of a chloride, as sodium chloride, be added. The precipitate obtained is the oxychloride and not the basic nitrate (*d*).

$$(a)\quad \mathrm{BiCl_3 + H_2O = \underbrace{BiOCl}_{} + 2HCl\,;}$$

$$(b)\quad \mathrm{Bi(NO_3)_3 + 2H_2O = Bi(OH)_2NO_3 + 2HNO_3\,;}$$

$$(c)\quad \mathrm{\underbrace{2Bi(OH)_2NO_3}_{} = (BiO)_2(OH)NO_3 + HNO_3 + H_2O\,;}$$

$$(d)\quad \mathrm{Bi(NO_3)_3 + NaCl + H_2O = \underbrace{BiOCl}_{} + NaNO_3 + 2HNO_3.}$$

The above precipitations are prevented by certain organic acids, as acetic, citric, etc.

The precipitates are easily soluble in HCl and HNO_3, but not in tartaric, the latter being a distinction from antimony.

Bismuth Sulphide (Bi_2S_3).—H_2S or soluble sulphides precipitate black bismuth sulphide from solutions of bismuth salts. The precipitate is insoluble in cold dilute acids and alkaline sulphides. Soluble in hot dilute nitric acid.

$$2Bi(NO_3)_3 + 3H_2S = \underbrace{Bi_2S_3} + 6HNO_3;$$

$$\underbrace{Bi_2S_3} + 8HNO_3 = 2Bi(NO_3)_3 + 2\overbrace{NO} + 4H_2O + \underbrace{3S}.$$

Bismuth Hydroxide ($Bi(OH)_3$).—Potassium, sodium, and ammonium hydrates give with solutions of bismuth salts a white precipitate of bismuth hydroxide, insoluble in excess of the reagents. The precipitation by ammonia is a distinction from copper and cadmium:

$$Bi(NO_3)_3 + 3KOH = Bi(OH)_3 + 3KNO_3$$

Tartaric acid, citric acid, and certain organic substances prevent the precipitation.

Bismuth Dioxide (Bi_2O_2).—If a solution of potassium stannite (made by adding KOH to stannous chloride until the precipitate which first forms has all dissolved) containing an excess of alkali be added to a solution of bismuth salt, a black precipitate of bismuth dioxide is formed. The reaction is delicate and, in absence of mercury salts, characteristic:

$$2Bi(NO_3)_3 + K_2SnO_2 + 6KOH \\ = \underbrace{Bi_2O_2} + K_2SnO_3 + 6KNO_3.$$

Bismuth Carbonate ($(BiO)_2CO_3$).—The alkaline carbonates precipitate bismuth salts, giving a basic carbonate.

Bismuth Chromate.—Soluble chromates precipitate bismuth solutions, giving yellow precipitates varying in composition according to conditions. With potassium dichromate it is $(BiO)_2Cr_2O_7$:

$$2Bi(NO_3)_3 + 3K_2Cr_2O_7 + 4H_2O \\ = (BiO)_2Cr_2O_7 + 6KNO_3 + 4H_2CrO_4.$$

Bismuth chromate is easily soluble in nitric acid, and insoluble in sodium or potassium hydrates (distinction from lead).

Reduction to Metal.—Bismuth is obtained from its solutions in the metallic state by addition of iron, zinc, etc., in the same way as for lead.

With sodium carbonate on charcoal, before the blowpipe the reaction is very similar to lead except that the bead is brittle.

COPPER (Cu). At. wt. 63.6; sp. gr. 8.9.

Copper has a characteristic red color, is very malleable and ductile, and is one of the best conductors of heat and electricity. Fuses at about 1100° C. It is contained in many important alloys, as bronze (Cu and Sn), brass (Cu and Zn), German silver (Cu Zn Ni), etc.

Copper dissolves easily in nitric acid (*a*), and is also soluble in hot concentrated sulphuric acid (*b*). Hydrochloric acid has very little action on it.

$$(a)\ 3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2\widetilde{NO} + 4H_2O\,;$$

$$(b)\ Cu + 2H_2SO_4 = CuSO_4 + \widetilde{SO_2} + 2H_2O.$$

Copper forms two oxides, the cuprous (Cu_2O) and cupric (CuO), and two corresponding series of salts. The cuprous salts are seldom met with, are unstable, and easily changed to cupric salt and metallic copper. They are nearly all insoluble in water.

Cupric Salts.—The ordinary copper salts all belong to this class. In the form of crystals or in solution they are of a green or blue color. The anhydrous salts are white.

Copper Sulphide.—H_2S and soluble sulphides precipitate cupric salts, giving a black precipitate of sulphide ($2CuS,Cu_2S$). This precipitate is easily soluble in hot dilute nitric acid, slightly soluble in ammonium sulphide, soluble in potassium cyanide (distinction from cadmium and all the other sulphides of the group), insoluble in boiling dilute sulphuric acid (another distinction from cadmium).

$$3(2CuS,Cu_2S) + 32HNO_3$$
$$= 12Cu(NO_3)_2 + 8\overbrace{NO} + \underbrace{9S} + 16H_2O;$$

Sodium thiosulphate ($Na_2S_2O_3$) in hot solutions of copper salts gives a black precipitate of cuprous sulphide. In solutions strongly acid with HCl this is a separation from cadmium.

Cupric Hydroxide ($Cu(OH)_2$).—Sodium or potassium hydrates precipitate from cupric solutions the blue hydroxide, insoluble in excess, soluble in ammonia and in acids.

On heating the precipitate, while still suspended in the liquid, it becomes black, changing to $3CuO,H_2O$.

In presence of sufficient tartaric, citric, or arsenious acids, grape-sugar, etc., the alkalies fail to give a precipitate, a blue solution being obtained.

If to the alkaline tartrate solution some grape-sugar be added and the solution boiled, a red or yellow precipitate of cuprous oxide is formed. This reaction is frequently used to determine the presence of grape-sugar in solutions.

Ammonium hydrate and carbonate when added to copper solutions gives at first a blue precipitate of a basic salt, which readily dissolves on further addition of ammonia to a deep-blue liquid. From copper sulphate the blue solution contains $CuSO_4,4NH_3 + H_2O$; with the chloride the solution contains $CuCl_2,4NH_3 + H_2O$.

Potassium cyanide decolorizes the blue solution, owing to the formation of double cyanide.

Cupric Carbonate.—The fixed alkaline carbonates precipitate from cupric solutions a greenish-blue basic carbonate of variable composition.

Cuprous Cyanide.—Potassium cyanide when added to cupric salts gives a precipitate of cuprous cyanide, or cuproso-cupric cyanide, easily soluble in excess.

Cupric Ferrocyanide (*Cu_2FeCy_6*).—Potassium ferrocyanide, when added to a solution of cupric salt gives a very characteristic reddish-brown precipitate of cupric ferrocyanide:

$$2CuSO_4 + K_4FeCy_6 = \underbrace{Cu_2FeCy_6} + 2K_2SO_4.$$

The precipitate is not affected by dilute acids, but it is decomposed by alkalies:

$$\underbrace{Cu_2FeCy_6}_{} + 4KOH = \underbrace{Cu(OH)_2}_{} + K_4FeCy_6.$$

Reduction to Metal.—Copper is easily precipitated in the metallic state, from its solutions, by iron, zinc, etc. A delicate and convenient way to make the test is to put a few drops of a dilute solution of copper in a platinum capsule, acidify with a drop of acid, and then add a small piece of zinc. The copper will usually be found adhering to the platinum, and can be recognized by its characteristic color.

Flame Test.—Copper salts, as well as the metal and its alloys, if held on a platinum wire in the flame of a Bunsen burner or blowpipe, color the flame green. Moistening the test with a drop of concentrated hydrochloric acid adds much to its delicacy. With the borax bead in the oxidizing flame copper compounds give a blue color

CADMIUM (Cd). At. wt. 112; sp. gr. 8.8.

Cadmium is a tin-white malleable metal, fusing at 315° C. It dissolves slowly in hot dilute hydrochloric or sulphuric acids with evolution of hydrogen. It is more easily soluble in nitric acid, which is its best solvent:

$$Cd + 2HCl = CdCl_2 + \overbrace{2H};$$

$$Cd + H_2SO_4 = CdSO_4 + \overbrace{2H};$$

$$3Cd + 8HNO_3 = 3Cd(NO_3)_2 + 2\overbrace{NO} + 4H_2O.$$

Cadmium resembles zinc in its chemical properties. It forms only one oxide, CdO, and a corresponding series of salts.

Cadmium Sulphide (*CdS*).—H_2S or soluble sulphides give with cadmium salts a yellow precipitate of sulphide, insoluble in cold dilute acids, alkaline sulphides, or potassium cyanide. Soluble in hot dilute nitric acid, also in boiling dilute sulphuric (the latter being a distinction from copper).

Cadmium Hydroxide (*Cd*(*OH*)$_2$).—Potassium and sodium hydrates precipitate cadmium solutions, giving a white hydrate, insoluble in excess of the alkali, soluble in acids.

With ammonium hydrate the same precipitate is formed, in absence of ammonium salts, which is very easily soluble in excess of ammonia.

Cadmium Carbonate (*CdCO*$_3$).—Potassium, sodium, and ammonium carbonates precipitate cadmium carbonate, white, insoluble in excess of the precipitant. Soluble in potassium cyanide. Free ammonia prevents the precipitation.

Cadmium Cyanide ($CdCy_2$).—Potassium cyanide gives with cadmium salts a white precipitate of cadmium cyanide, easily soluble in excess of reagent, forming double cyanide. From this solution the cadmium is precipitated by H_2S as sulphide:

$$Cd(NO_3)_2 + 2KCy = \underbrace{CdCy_2} + 2KNO_3;$$

$$\underbrace{CdCy_2} + 2KCy = CdCy_2,2KCy;$$

$$CdCy_2,2KCy + 2H_2S = \underbrace{CdS} + 4\overbrace{HCy} + K_2S.$$

Blowpipe Test.—Cadmium compounds fused on charcoal with dry sodium carbonate are reduced to metal, which volatilizes and forms a characteristic brown coat on the coal.

RECAPITULATION.

On reviewing the reactions of the metals of the fifth group we at once see that they differ from all of the metals of the preceding groups in the fact that they are precipitated from solutions acid with the strong acids, by H_2S, and it will be found later on that they differ from the sixth group in the insolubility of their sulphides in alkaline sulphides, the sixth-group sulphides being soluble.

A further distinction in regard to three of the metals (Ag, Pb, Hg (ous)) is found in the insolubility of their chlorides in dilute hydrochloric acid. This reaction enables us to separate these metals, not only from those of all the other groups, but also from the remaining metals of the fifth.

Let us suppose, for example, that we have a solution containing metals of all six groups; hydrochloric acid is added to it in slight excess, and the mixture filtered. The precipitate will contain silver, lead, and mercurous chlorides, and in the filtrate will be all of the other metals. This filtrate is now acid with hydrochloric acid, owing to the fact that more than sufficient to precipitate the chlorides was used in the first precipitation. If now we add H_2S in excess to the solution, the remainder of the fifth group and all of the sixth will precipitate. On filtering, these metals will be separated from those of the first four groups, which will be found in the filtrate.

If now we make use of the fact that the fifth group sulphides are insoluble in ammonium sulphide, and those of the sixth soluble, we can easily separate one from the other. Doing this, we have a residue containing the second division of the fifth group (Pb (?), Hg (ic), Bi, Cu, Cd) and in the filtrate the sixth group as sulphur salts.

Going back now to our precipitate of the chlorides ($AgCl, PbCl_2, Hg_2Cl_2$) we see, on studying their properties, several points in which they differ from each other. Lead chloride, for example, is soluble in boiling water, the others insoluble: if, then, we treat a precipitate of the three with hot water, the lead chloride will all be dissolved, and on filtering will be found in the filtrate, where its presence may be proved by adding sulphuric acid, which, as we already know, precipitates lead and no other metal of the group.

In the residue left after removal of the lead chloride we have only silver and mercurous chlorides, which, you will remember, differ from each other in their action with ammonia, the silver chloride being soluble, and the other not only insoluble, but it changes in color from white to black, which change is characteristic for mercurous salt.

From the ammoniacal solution, you know, the silver chloride can be reprecipitated by acidifying with nitric acid. By this series of reactions we have separated these three metals from all of the groups and from each other. Let us return to our residue of sulphides (PbS (?), HgS, Bi_2S_3, Cu_4S_3, and CdS), and see in what way it can be separated. Hot dilute nitric acid will dissolve all of these, with the exception of the mercuric sulphide (HgS); so if we boil the residue with dilute nitric acid, the lead, bismuth, copper, and cadmium sulphides go into solution as nitrates, and the HgS remains insoluble, which after filtering can be dissolved in a little aqua regia (*i.e.*, Cl), and on the solution of mercuric chloride obtained any of the characteristic tests for mercury may be made—preferably the precipitation with stannous chloride ($SnCl_2$).

In the filtrate containing the nitrates it is always necessary to look for lead, since, owing to its being somewhat soluble in water, a portion is always likely to be found at this point. Making use of the action of sulphuric acid on lead salts, we can readily remove any lead that may be present.

Filtering, only bismuth, copper, and cadmium are left. The action of ammonia on these salts enables us at once to separate the bismuth as hydroxide, the copper and cadmium going into solution as ammonia compounds—copper, if present, giving the solution its characteristic blue color. As the formation of a white precipitate on the addition of ammonia is not conclusive proof of the presence of bismuth, it is always necessary to dissolve the precipitate in a little dilute hydrochloric acid and make the very characteristic water test.

The copper and cadmium may be determined in the ammoniacal solution by the reactions with cyanides.

If further test for copper besides the blue color of the solution is desired, it is made by acidifying a portion of the solution with acetic acid, and then adding potassium ferrocyanide, copper, if present, giving its well-known red ferrocyanide.

You perhaps remember that copper sulphide is soluble in potassium cyanide, and that cadmium sulphide is insoluble, if, then, we add sufficient of the cyanide to change the copper and cadmium to double cyanides, and pass H_2S into this solution, the cadmium is precipitated as yellow sulphide.

We might make use of some of the other reactions of these metals, as the action of hot dilute sulphuric acid on the sulphides, to effect their separation, but the one with the cyanide is reliable and easy to perform.

In Scheme No. V the plan adopted is that just outlined.

METALS OF THE SIXTH GROUP.

TIN, ARSENIC, ANTIMONY, GOLD, AND PLATINUM.

THESE metals, like those of Group V, are precipitated by H_2S from acid solutions, but differ from the latter in the solubility of the sulphides in alkaline sulphides, with formation of soluble thio-salts.

The metals of this group may be conveniently divided into two divisions: arsenic, antimony, and tin comprising the first, and gold and platinum the second. Those of the first division form oxides, stable at a high temperature, while those of the second are characterized by the easy reduction to metal of all their compounds. The sulphides of gold and platinum are insoluble in either boiling hydrochloric or nitric acids, which is a distinction from the sulphides of arsenic, antimony, and tin.

Thio-salts.—These salts of the sixth group are of so much importance that it will be best to try and get a clear conception of their character before proceeding any further.

Tin, antimony, and arsenic form two series of oxides; viz., stannous (SnO), stannic (SnO_2), antimonious (Sb_4O_6), antimonic (Sb_2O_5), arsenious (As_4O_6), and arsenic (As_2O_5). These oxides act as the anhydrides of corresponding acids, *e.g*, arsenious acid, H_3AsO_3 ($As_4O_6 + 6H_2O = 4H_3AsO_3$), arsenic acid, H_3AsO_4 ($As_2O_5 + 3H_2O = 2H_3AsO_4$). Stannous oxide generally acts as a base, but in a few compounds it plays the part of a weak acid corresponding to H_2SnO_2. Stannic oxide is more distinctly acid in its properties, and much more stable, and forms the acid H_2SnO_3. The two oxides of antimony act in much the same way as tin, only the acid characteristics are more decided.

There is a corresponding series of sulphides, viz., SnS, SnS_2, Sb_2S_3, Sb_2S_5, As_2S_3, As_2S_5.

These sulphides, particularly the higher ones, correspond in many ways with the anhydrides of the acids just spoken of, combining with other sulphides to form salts, in the same way that the oxides do; *e.g.*,

$$3K_2O + As_2O_5 = 2K_3AsO_4.$$

Now suppose the oxygen in this equation to be replaced by sulphur, and we get the equation

$$3K_2S + As_2S_5 = 2K_3AsS_4 \text{ (potassium thio-arsenate).}$$

Antimony sulphide forms a similar compound, $(NH_4)_3SbS_4$, corresponding to ortho-antimonic acid (H_3SbO_4).

Stannic oxide combines with oxides of the metals to form stannates, such as

$$K_2O + SnO_2 = K_2SnO_3.$$

If we treat this equation as we did the previous one and replace all the oxygen with sulphur, we have

$$K_2S + SnS_2 = K_2SnS_3 \text{ (potassium thio-stannate).}$$

It is evident from this comparison that the thio-salts correspond to the oxygen compounds, sulphur replacing oxygen atom for atom. Many of the thio-salts are much more complex than the examples given, and correspond to the meta- and pyro-salts of the oxygen acids, *e.g.*, $Na_4As_2S_7$ (sodium pyro-thio-arsenate), corresponding to $Na_4As_2O_7$.

TIN (Sn). At. wt. 119; sp. gr. 7.3.

Tin is a white, lustrous, and malleable metal, fusing at 235° C. Fused in the air, it is rapidly changed to oxide, forming a white powder used for polishing, under the name of putty powder. Its best solvent is hot strong hydrochloric acid, in which it dissolves to stannous chloride ($SnCl_2$) (*a*). Aqua regia or chlorine dissolves it readily, forming stannic chloride ($SnCl_4$) (*b*). With nitric acid the action varies according to the strength of acid. Strong acid yields metastannic acid ($H_{10}Sn_5O_{15}$), insoluble in acids and in water (*c*); dilute acid gives either stannous nitrate ($Sn(NO_3)_2$), stannic nitrate ($Sn(NO_3)_4$), or a mixture of the two, depending on temperature and strength of the acid.

In dilute sulphuric acid it is very slowly soluble, but dissolves in concentrated acid to stannic sulphate.

(*a*) $Sn + 2HCl = SnCl_2 + \overset{\cdot\cdot}{\widetilde{H_2}}$;

(*b*) $Sn + 2Cl_2 = SnCl_4$;

(*c*) $15Sn + 20HNO_3 + 5H_2O = 3H_{10}Sn_5O_{15} + 20\widetilde{NO}$.

Tin is a constituent of many important alloys, as bronze, solder, etc.; and it is also largely used in the manufacture of tin-plates, which are iron plates coated with tin.

Tin forms two oxides, stannous (SnO) and stannic (SnO_2), and corresponding salts.

Stannous Salts.—Stannous salts oxidize very easily to stannic, and consequently are strong reducing agents. On exposure to air, stannous chloride, for example, oxidizes to stannic oxychloride (Sn_2OCl_2). Chlorine or strong nitric acid easily effects its oxidation.

Many other substances, as ferric salts, mercury salts, etc., act in the same way:

$$SnCl_2 + Fe_2Cl_6 = 2FeCl_2 + SnCl_4.$$

Reactions with mercury and bismuth salts have already been given.

Stannous Hydroxide (*$Sn(OH)_2$*).—The alkaline hydrates and carbonates give with solutions of stannous salts a white precipitate of stannous hydrate.

The precipitate is soluble in excess of sodium or potassium hydrate and in acids.

$$SnCl_2 + 2KOH = \underbrace{Sn(OH)_2} + 2KCl;$$

$$Sn(OH)_2 + 2KOH = K_2SnO_2 + 2H_2O.$$

Stannous Sulphide (*SnS*).—Stannous salts yield with H_2S a brown precipitate of stannous sulphide (*a*), insoluble in dilute acids and in colorless ammonium sulphide and in ammonium carbonate.

It is soluble in potassium or sodium hydrates and, as already explained, in alkaline polysulphides, with formation of a thio-stannate of the alkali (*b*).

From its solution in alkali or alkaline sulphide it is reprecipitated by acids (*c*).

Stannous sulphide is soluble in hot strong hydrochloric acid, with evolution of H_2S (*d*).

Concentrated nitric acid converts it into metastannic acid:

(*a*) $SnCl_2 + H_2S = \underbrace{SnS} + 2HCl;$

(*b*) $\underbrace{SnS} + (NH_4)_2S_2 = (NH_4)_2SnS_3;$

(*c*) $(NH_4)_2SnS_3 + 2HCl = \underbrace{SnS_2} + \overbrace{H_2S} + 2NH_4Cl;$

(*d*) $\underbrace{SnS} + 2HCl = SnCl_2 + \overbrace{H_2S}.$

Reducing Action.—The reducing action of stannous salts gives us several valuable qualitative reactions for tin, when it is present in the stannous condition. It must be remembered, however, that, since these reactions depend on the stannous salt reducing the reagent added, the result is not conclusive, unless we know that no other reducing agent is present.

The reactions between stannous and mercury salts have already been given under the head of Mercury. Of course, when used as a test for tin we simply reverse the method of procedure, and add a solution of a mercury salt (preferably mercuric chloride) to the solution we wish to test, remembering that if the mercury salt is added in excess we get only a reduction to mercurous chloride, a white precipitate:

$$SnCl_2 + 2HgCl_2 = \underbrace{Hg_2Cl_2}_{} + SnCl_4.$$

Another very delicate test is made by adding to a dilute solution of ferric chloride and potassium ferricyanide a solution containing stannous salt. A blue precipitate of ferrous ferricyanide is at once formed, owing to the stannous salt reducing the ferric salt, which is then precipitated by the ferricyanide:

(*a*) $3Fe_2Cl_6 + 3SnCl_2 = 6FeCl_2 + 3SnCl_4;$

(*b*) $6FeCl_2 + 3SnCl_4 + 2K_6(FeCy_6)_2$

$$= 2Fe_3(FeCy_6)_2 + 12KCl + 3SnCl_4.$$

The reaction with bismuth salts might also be made use of as a test for tin (see Bismuth).

The reduction of tin to the metallic state will be spoken of under the head of Stannic Salts.

STANNIC SALTS.

Stannic oxide forms two hydrates, stannic acid (H_2SnO_3) and metastannic acid ($H_{10}Sn_5O_{15}$); these hydrates unite with both bases and acids to form salts. Stannic acid is soluble in acid, forming salts, such as stannic chloride ($SnCl_4$), and in sodium or potassium hydrates, yielding stannates, as Na_2SnO_3.

Metastannic acid is insoluble in acids, and is difficultly soluble in sodium or potassium hydrates. If it is boiled with strong hydrochloric acid, no apparent action takes place; but if the acid be poured off, and water added to the residue, it goes into solution as metastannic chloride.

In order to prepare stannic chloride free from the metastannate, metallic tin should be dissolved in strong hydrochloric acid, and some potassium chlorate then added, and the solution boiled again, so as to oxidize the stannous chloride first formed to stannic chloride. Solutions of stannic salt change on standing to metastannate, the action being rapid in hot solutions, and slow in cold.

Solutions of the alkalies and alkaline carbonates precipitate both stannic and metastannic salts as stannic or metastannic acid. The former is soluble in the fixed alkalies, if the latter are not added in too great excess. It is also soluble in acid.

$$SnCl_4 + 4KOH = \underbrace{H_2SnO_3} + 4KCl + H_2O;$$

$$\underbrace{H_2SnO_3} + 2KOH = K_2SnO_3 + 2H_2O.$$

Stannic Sulphide (*SnS_2*).—H_2S precipitates stannic or metastannic solutions if they are not too acid, giving a precipitate of stannic sulphide (*a*), which is white at first but finally changes to yellow. To insure complete precipitation, the acid present must be very dilute. Heating gently helps the reaction.

The precipitate is soluble in alkaline sulphides (*b*), in sodium and potassium hydrates, and in boiling hydrochloric acid (*d*), or aqua regia. From its solution in alkali or alkaline sulphide it is reprecipitated on the addition of acid (*c*). It is insoluble in ammonia and ammonium carbonate (distinction from arsenic). Nitric acid changes it to metastannic acid.

$$(a)\ SnCl_4 + 2H_2S = \underline{SnS_2} + 4HCl;$$

$$(b)\ \underline{SnS_2} + (NH_4)_2S = (NH_4)_2SnS_3;$$

$$(c)\ (NH_4)_2SnS_3 + 2HCl = \underline{SnS_2} + 2NH_4Cl + H_2S;$$

$$(d)\ \underline{SnS_2} + 4HCl = SnCl_4 + 2H_2S.$$

Precipitation of Stannic Salts as Metastannic Acid.—The conversion of a stannic salt into metastannic acid affords us one of the best methods of determining stannic salts, particularly in presence of stannous. The change is easily effected in the following manner:

To a solution containing stannic salt, which must be only very faintly acid, is added a strong solution of sodium sulphate or ammonium nitrate, and heat applied; metastannic acid quickly precipitates as a white precipitate.

Metastannic solutions are precipitated by the same reagents:

$$5SnCl_4 + 20Na_2SO_4 + 15H_2O = \underline{H_{10}Sn_5O_{15}} + 20NaCl + 20NaHSO_4.$$

$$5SnCl_4 + 20NH_4NO_3 + 15H_2O = H_{10}Sn_5O_{15} + 20NH_4Cl + 20HNO_3.$$

Tin is easily obtained in the metallic state from all its solutions by the addition of zinc. The tin precipitates as a gray, spongy mass.

$$SnCl_2 + Zn = \underline{Sn} + ZnCl_2.$$

Tinstone (SnO_2), or metastannic acid, can be reduced in the same way. The test is best made in presence of platinum. Place the tin ore, which should be very finely pulverized, in a test-tube, add a piece of platinum-foil and a few small pieces of zinc, then cover with strong hydrochloric acid, and boil. The tin will be obtained as a spongy mass.

Tin when precipitated in contact with platinum does not stain the platinum black (a distinction from antimony).

If a compound of tin be mixed with sodium carbonate or potassium cyanide, and heated on charcoal in the reducing-flame, before the blowpipe, the tin is obtained in lustrous, malleable globules. Near the test will be found a white coating of stannic oxide. If this be moistened with a drop of nitrate of cobalt and again ignited it gives a green color.

ANTIMONY (Sb). At. wt. 120.4; sp. gr. 6.7.

Antimony is a lustrous, bluish white, brittle *metal,* fusing at 425° C. It is only very slightly acted on by air at the ordinary temperature; but if heated to redness it takes fire, giving off white fumes of antimonious oxide.

It is only very slightly soluble in hydrochloric or sulphuric acids. Nitric acid converts it either into antimonious oxide (Sb_4O_6) (*a*), or antimonic anhydride (Sb_2O_5) (*b*). Chlorine or aqua regia dissolves it, forming antimonious chloride ($SbCl_3$). If dissolved in aqua regia the nitric acid should be added only a little at a time, otherwise insoluble oxides will be formed. Boiling tartaric acid dissolves precipitated antimony slowly (*c*).

$$(a)\ 4Sb + 4HNO_3 = \underbrace{Sb_4O_6} + 4\overbrace{NO} + 2H_2O\,;$$

$$(b)\ 6Sb + 10HNO_3 = 3\underbrace{Sb_2O_5} + 10\overbrace{NO} + 5\,H_2O\,;$$

$$(c)\ 2Sb + H_2C_4H_4O_6 + 2H_2O = (SbO)_2C_4H_4O_6 + 3\overbrace{H_2}.$$

Antimony forms two oxides—antimonious and antimonic: the first acts as a weak base, the latter as an acid anhydride forming the acids H_4SbO_4 (orthoantimonic), $H_4Sb_2O_7$ (pyroantimonic), and $HSbO_3$ (metantimonic).

The commonly occurring salts of antimony are those formed from antimonious oxide.

Antimonious oxide is soluble in hydrochloric, sulphuric, and tartaric acids, but not in nitric.

Antimonious Hydroxide.—The alkalies and alkaline carbonates give in antimonious solutions a white precipitate of antimonious hydroxide ($SbO(OH)$), soluble in excess of the fixed alkalies, and in hot sodium or potassium carbonates; also soluble in acids, with the exception of nitric. Tartaric acid or tartrates interfere with or prevent the reaction.

Antimony Sulphide.—H_2S added to slightly acid solutions containing antimony, either as antimonious or antimonic compounds, give an orange-red precipitate of antimonious or antimonic sulphide (*a*). The precipitate is easily soluble in the fixed alkalies and in alkaline polysulphides (*b*), from which solutions it is reprecipitated on the addition of acids as antimonic sulphide (Sb_2S_5) (*c*).

It is soluble in hot strong hydrochloric acid, with evolution of H_2S (*d*).

In ammonia and ammonium carbonate it is nearly insoluble (a distinction from arsenic).

(*a*) $2SbCl_3 + 3H_2S \quad = \underbrace{Sb_2S_3} + 6HCl;$

(*b*) $\underbrace{Sb_2S_3} + 3(NH_4)_2S_2 = 2(NH_4)_3SbS_4 + S;$

$$
\begin{aligned}
&(c)\ 2(NH_4)_3SbS_4 + 6HCl \\
&\qquad\qquad = \underbrace{Sb_2S_5} + 6NH_4Cl + 3\overbrace{H_2S}\,; \\
&(d)\ \underbrace{Sb_2S_3} + 6HCl \quad = 2SbCl_3 + 3\overbrace{H_2S}.
\end{aligned}
$$

Precipitation by Water.—The action of water on antimony solutions is very characteristic. If to a solution of antimonious chloride an excess of water be added, a white precipitate of oxychloride will be obtained, which differs from the bismuth oxychloride in being soluble in tartaric acid. Like the bismuth precipitate, it is soluble in hydrochloric acid. The precipitate is best obtained in a solution not strongly acid.

Tartaric and citric acids prevent the precipitation:

$$SbCl_3 + H_2O = \underbrace{SbOCl} + 2HCl.$$

Metallic Antimony.—In solutions free from nitric acid zinc precipitates metallic antimony in the form of a black powder. If the precipitation be made in a platinum capsule, the antimony precipitates on the platinum as a black or brownish-black adherent coating, very slightly soluble in hydrochloric acid (a distinction from arsenic and tin).

The test is shown even by very dilute solutions, and is very characteristic for antimony.

Antimony Hydride (SbH_3).—When zinc is added to acid solutions containing antimony, the hydrogen liberated unites with the antimony and forms the hydride, SbH_3 (*a*) (also called antimonetted hydrogen, or stibine). If the test be made in a small flask fitted with a delivery-tube, the gas may be lighted. (Care should be taken to have all the air expelled before igniting the gas, otherwise an explosion may result.) It burns with a bluish-violet flame, evolving heavy fumes of antimonious oxide (*b*). If a piece of cold porcelain be held in the flame, the hydride is decomposed, and metallic antimony is deposited on the porcelain as a black spot. It is dull black and lustreless, and insoluble in sodium hypochlorite ($NaClO$) (a distinction from arsenic).

Antimony hydride when passed into a solution of silver nitrate gives a black precipitate of silver antimonide (Ag_3Sb) (*c*) (a distinction from arsenic).

This precipitate is soluble in tartaric or hydrochloric acids (*d*), from which solution, after acidifying with hydrochloric acid, it may be precipitated as the characteristic red sulphide.

$$(a)\ SbCl_3 + 3Zn + 3HCl = \overbrace{SbH_3} + 3ZnCl_2;$$

$$(b)\ 4SbH_3 + 6O_2 = Sb_4O_6 + 6H_2O;$$

$$(c)\ SbH_3 + 3AgNO_3 = \underbrace{Ag_3Sb} + 3HNO_3;$$

$$(d)\ 2Ag_3Sb + H_2C_4H_4O_6 + 2H_2O$$
$$= (SbO)_2C_4H_4O_6 + \overbrace{3H_2} + \underbrace{6Ag}.$$

Blowpipe Test.—If any compound of antimony be mixed with dry sodium carbonate and potassium cyanide, and fused on charcoal before the blowpipe, in the reducing-flame, the antimony is reduced to a metallic globule, which rapidly oxidizes, and forms a heavy deposit of oxide on the coal.

ARSENIC (As). At. wt. 75; sp. gr. 5.7.

Arsenic stands on the border-line between the metals and non-metals. In its elemental form it has more of the characteristics of a metal, but in nearly all of its compounds it acts as an acid. In appearance it is gray, with a metallic lustre, and is very brittle. It volatilizes easily, without fusion, when heated to a dull red.

Heated in the air, it gives a characteristic garlic odor, and if heated to a high temperature with free access of air, it burns to arsenious oxide (As_2O_3).

Arsenic is insoluble in hydrochloric and dilute sulphuric acids. Hot concentrated sulphuric acid converts it into arsenious acid. On heating with nitric acid it forms either arsenious or arsenic oxides, depending on the strength of the acid. Its best solvent is aqua regia or chlorine, in which it easily dissolves as arsenic acid (H_3AsO_4):

$$2As + 5Cl_2 + 8H_2O = 2H_3AsO_4 + 10HCl.$$

Arsenious Oxide (As_4O_6).—This oxide is either crystalline or amorphous, and when heated easily volatilizes. It is only slightly soluble in cold water, but dissolves more readily in hot. Hydrochloric acid and the alkalies dissolve it without difficulty. If the hydrochloric acid solution be evaporated, arsenious chloride volatilizes.

Arsenious acid is a very weak acid. Its only soluble salts are those of the alkalies. All of the insoluble arsenites are dissolved or decomposed by hydrochloric acid.

Arsenious Sulphide (As_2S_3).—H_2S added to aqueous solutions of arsenious acid or alkali arsenites gives no precipitate, the arsenious sulphide produced assuming the colloidal form; but if the solution be made acid with a strong acid, as hydrochloric, the sulphide is at once thrown down as a yellow precipitate (*a*).

Alkaline sulphides (*b* and *d*), hydrates, and carbonates (*f*) dissolve it readily. Acids reprecipitate it from these solutions (*c*, *e*, *g*). Its solubility in ammonium carbonate is a distinction between it and antimony and tin sulphides.

Its insolubility in hydrochloric acid, even on boiling, affords another way of separating it from the same metals.

(*a*) $$2H_3AsO_3 + 4HCl + 3H_2S = As_2S_3 + 6H_2O + 4HCl;$$

(*b*) $$\underbrace{As_2S_3} + 3(NH_4)_2S = 2(NH_4)_3AsS_3;$$

(*c*) $$2(NH_4)_3AsS_3 + 6HCl = \underbrace{As_2S_3} + 6NH_4Cl + 3\overbrace{H_2S};$$

(*d*) $$\underbrace{As_2S_3} + 3(NH_4)_2S_2 = 2(NH_4)_3AsS_4 + S;$$

(*e*) $$2(NH_4)_3AsS_4 + 6HCl = \underbrace{As_2S_5} + 6NH_4Cl + 3\overbrace{H_2S};$$

(*f*) $$\underbrace{2As_2S_3} + 2(NH_4)_2CO_3 = NH_4AsO_2 + 3NH_4AsS_2 + 2\overbrace{CO_2};$$

(*g*) $$NH_4AsO_2 + 3NH_4AsS_2 + 4HCl = \underbrace{2As_2S_3} + 4NH_4Cl + 2H_2O.$$

Silver Arsenite (Ag_3AsO_3).—If silver nitrate be added to a solution of an arsenite, it produces a yellow precipitate of silver arsenite. In aqueous solutions of arsenious acid no precipitate is formed; but if dilute ammonia be carefully added, the precipitate forms at once.

The precipitate is very easily soluble in nitric acid and in ammonia, and is somewhat soluble in ammonium nitrate:

$$K_3AsO_3 + 3AgNO_3 = \underbrace{Ag_3AsO_3} + 3KNO_3.$$

Cupric Arsenite ($CuHAsO_3$).—Cupric sulphate added to a solution of an arsenite produces a yellowish-green precipitate of arsenite, easily soluble in acids and alkalies:

$$K_3AsO_3 + CuSO_4 + H_2O$$
$$= \underbrace{CuHAsO_3} + K_2SO_4 + KOH.$$

If the solution containing the arsenite be made strongly alkaline with potassium hydrate, and then only a few drops of a weak solution of cupric sulphate be added, and the solution boiled, a red precipitate of cuprous oxide is obtained:

$$K_3AsO_3 + 2CuSO_4 + 4KOH$$
$$= \underbrace{Cu_2O} + K_3AsO_4 + 2K_2SO_4 + 2H_2O.$$

This test is not conclusive for arsenic, since grape-sugar and other organic substances give the same precipitate. It is, however, valuable as a confirmatory test and as a means of distinguishing between arsenious and arsenic acid. As the reaction depends on the oxidation of the arsenite to arsenate, it is evident that the latter could not give the reaction.

ARSENIC OXIDE.

Arsenic oxide is a white amorphous solid, fusing at a red heat, and at higher temperatures it volatilizes as arsenious oxide and oxygen. It is slowly soluble in cold water, more easily in hot, going into solution as orthoarsenic acid (H_3AsO_4).

Arsenic acid is very similar in many ways to phosphoric acid. Like the latter it forms pyro and meta acids, and the solubility of its salts is much the same. The only arsenates soluble in water are those of the alkalies. Arsenic acid, like arsenious, is a poison.

Arsenic Sulphide.—H_2S does not precipitate neutral or alkaline solutions of arsenates, and in acid solutions no precipitate is formed at first, but after long standing one is slowly formed, consisting of a mixture of arsenic and arsenious sulphides and sulphur. If the solution be moderately acid, and heated to 70° C., and a strong current of H_2S be passed into it, the precipitate will be principally arsenic sulphide.

When admissible arsenates can be very readily precipitated as sulphide, by first reducing the arsenate to arsenite by adding sulphurous acid (*a*), or, what is equivalent, a sulphite to an acid solution (*b*), warming, and then precipitating with H_2S.

$$(a)\ K_3AsO_4 + SO_2 + H_2O = K_3AsO_3 + H_2SO_4;$$

$$(b)\ Na_2SO_3 + 2HCl \qquad = \widetilde{SO_2} + 2NaCl + H_2O$$

It is seen from (*a*) that sulphuric acid is produced by the reduction of the arsenate, consequently in any solution containing metals forming insoluble sulphates, this method could not be used to advantage. The solubilities of arsenic sulphide are analogous to those of arsenious sulphide already given.

Silver Arsenate (Ag_3AsO_4).—Silver nitrate added to solutions of arsenic acid or arsenates gives a reddish brown precipitate of arsenate. The precipitate is easily soluble in nitric acid and ammonia, and also somewhat soluble in ammonium *nitrate.*

Magnesium Ammonium Arsenate.—If to a solution of arsenic acid or an arsenate soluble in water a mixture of magnesium sulphate, ammonium chloride, and excess of ammonia (known as magnesium mixture) be added, a white crystalline precipitate of magnesium ammonium arsenate is obtained. It is easily soluble in acids. If a small portion of the washed precipitate be placed on a watch-glass and dissolved in a drop of dilute nitric acid, silver nitrate added, and the solution obtained neutralized very cautiously with ammonia, the characteristic red arsenate of silver is precipitated :

$$K_3AsO_4 + MgCl_2,NH_4Cl + NH_4OH \\ = MgNH_4AsO_4 + 3KCl + NH_4OH.$$

Hydrogen Arsenide (AsH_3).—If a solution of arsenious or arsenic acid or any of their compounds (except sulphides) be treated with zinc and dilute sulphuric or hydrochloric acids in the same manner as given for antimony, gaseous hydrogen arsenide will be formed (*a*), which can be ignited in the same way as the antimony compound, giving the flame a bluish tint, and white fumes of arsenious oxide are formed (*b*). If a piece of cold porcelain be held in the flame, a brownish-black stain of solid hydrogen arsenide, having a decided lustre, is obtained. The deposit, unlike that of antimony, is soluble in sodium hypochlorite (*c*). When arsenic and antimony are present together, the use of sodium hypochlorite as a means of separation is not reliable. A better plan is to add a drop or two of ammonium sulphide to the black stain obtained, evaporate at a gentle heat, and then place the piece of porcelain with the stain, now changed to sulphide, downward, over a small beaker containing fuming hydrochloric acid. If antimony only is present, the orange-colored residue disappears, volatilizing as chloride; but if arsenic be present, the yellow arsenious sulphide remains (ANDERSON).

If hydrogen arsenide be passed into a solution of silver nitrate, a black precipitate of metallic silver is formed, and the arsenic goes into solution as arsenious oxide (*d*). After filtering out the silver, the arsenic may be precipitated in the filtrate as silver arsenite, by adding a few drops of silver nitrate, and then neutralizing *very carefully* with dilute ammonia (*e*).

(*a*) $H_3AsO_3 + 3Zn + 6HCl$

$$= \overbrace{AsH_3} + 3ZnCl_2 + 3H_2O;$$

(*b*) $4AsH_3 + 6O_2 = As_4O_6 + 6H_2O$;

(*c*) $2AsH_3$ (solid hydride, or stain) $+ 8NaClO$
$= 2H_3AsO_4 + 8NaCl$;

(*d*) $AsH_3 + 6AgNO_3 + 3H_2O$
$= H_3AsO_3 + 6\underbrace{Ag} + 6HNO_3$;

(*e*) $H_3AsO_3 + 6HNO_3 + 3AgNO_3 + 9NH_4OH$
$= \underbrace{Ag_3AsO_3} + 9NH_4NO_3 + 9H_2O$.

Reduction to Metallic Arsenic.—If arsenites, arsenates, or the sulphides are fused with a mixture of three parts of sodium carbonate and one of potassium cyanide, the arsenic is reduced to the metallic form. The test is made in a glass tube blown into a small bulb at one end, the mixture is introduced into the bulb and heated, the reduced arsenic volatilizes, and condenses as a dark mirror in the upper part of the tube.

If any compound of arsenic be mixed with sodium carbonate, and fused on charcoal in the reducing-flame of the blowpipe, the highly characteristic garlic odor will be observed.

GOLD (Au). At. wt. 197.2; sp. gr. 19.3.

Gold is a yellow metal, very lustrous, soft, and exceedingly malleable. Precipitated from solution it varies in color from brown to nearly black. It fuses only at a high temperature (about 1035° C.), and does not oxidize upon ignition in the air.

It is insoluble in any of the acids alone, but dissolves easily in aqua regia or any solution containing chlorine, yielding a solution of auric chloride ($AuCl_3$). Solutions containing free bromine or iodine also dissolve it.

The alkaline cyanides in presence of air or oxygen dissolve gold, and although the action is slow, it is of great commercial importance, a very large amount of gold being obtained from its ores by leaching them with a solution of potassium cyanide:

$$4Au + 8KCy + O_2 + 2H_2O = 4KAuCy_2 + 4KOH.$$

It is not attacked by fusion with acid potassium sulphate (a distinction from almost all of the metals).

Gold is found very widely distributed in nature, although as a rule in very small quantities. It is almost always found in the metallic state alloyed with more or less silver. Iron and copper pyrites often contain it, and it is a disputed point as to whether the gold is there present as a sulphide or in the metallic state. Tellurium combines with gold to form a telluride. Gold forms a considerable number of double salts, as $KAuCl_4$, $KAuCy_2$, etc.

Strong ignition decomposes all gold salts, leaving a residue containing metallic gold.

Oxides.—There are two oxides of gold, aurous, Au_2O, and auric, Au_2O_3, and two corresponding series of salts.

Both of the oxides are dark brown or black, and decompose on ignition into metal and oxygen. They dissolve readily in hydrochloric acid, but not in sulphuric or nitric. Aurous chloride is decomposed by water into auric chloride and metallic gold.

Auric chloride is soluble in water, giving a reddish-brown color in concentrated solutions and yellow in dilute, the color being visible even when greatly diluted.

Action of the Alkalies.—Potassium hydrate in very concentrated solution gives a brown precipitate that dissolves in excess of the reagent, forming potassium aurate, $K_2Au_2O_4$.

Ammonia gives in concentrated solutions a reddish-yellow precipitate of auric oxide combined with NH_3, called " fulminating gold.

Auric oxide is most readily obtained by precipitating with magnesia (MgO) or its hydroxide.

Gold Sulphide.—H_2S in neutral or acid solutions gives a brownish-black precipitate which is said to be Au_2S_2 when precipitated from cold solutions, and a mixture of the same with metallic gold and sulphur if the solution is hot. The precipitate is insoluble in hydrochloric and nitric acids even on heating, but is soluble in aqua regia (Cl). It is also soluble in the alkaline sulphides, particularly on heating; at least that portion which is present as sulphide is dissolved.

Ammonium sulphide also precipitates gold as Au_2S_2, soluble in an excess of the reagent.

Reduction to the Metallic State.—Gold is easily reduced to the metallic state from its solutions by many different reagents, among the most important being ferrous and stannous salts, oxalic acid, sulphurous acid (in hot solution), and the metals, particularly zinc.

Action of Ferrous Salts.—Ferrous salts when added to solutions containing gold as chloride or bromide give a dark-brown precipitate of me- llic gold. The solution containing the sus- ed precipitate has a characteristic blue-black color, especially if the original solution was very dilute.

$$2AuCl_3 + 6FeSO_4 = 2Au + 2Fe_2(SO_4)_3 + Fe_2Cl_6.$$

Oxalic Acid, when added to a solution of the chloride or bromide, which must be free from nitric acid, and contain little or no hydrochloric, gives on warming the solution a precipitate of metallic gold which separates in flakes or is deposited as a mirror on the sides of the vessel.

$$2AuCl_3 + 3H_2C_2O_4 = 2Au + 6\overbrace{CO}_2 + 6HCl.$$

Stannous Chloride containing a little stannic salt gives in dilute acid or neutral solutions of gold a brown or purple precipitate ("purple of Cassius").

Potassium nitrite also precipitates gold in the metallic state, even from very dilute solutions.

Metallic Zinc is a very valuable precipitant for gold, precipitating it not only from acid solutions, but also from its solution in cyanides:

$$2KAuCy_2 + Zn = \underbrace{2Au} + 2KCy,ZnCy_2.$$

Mercury.—Gold dissolves readily in mercury, forming an amalgam from which the gold can be easily regained by ignition, the mercury volatilizing.

This is the basis of the well-known amalgamation process for the extraction of gold from its ores.

PLATINUM (Pt). At. wt. 194.9; sp. gr. 21.5.

Platinum when compact is of a steel-gray color, is exceedingly malleable and ductile, and very infusible. Precipitated platinum is black. Its fusing-point is about 1775° C.; ignition in the air does not alter it. Like gold, it is insoluble in any one of the acids, and also when fused with acid potassium sulphate.

It is soluble in aqua regia or chlorine, the solution consisting of hydrochloroplatinic acid (H_2PtCl_6).

The alkaline nitrates and their hydroxides with access of air oxidize platinum at a red heat. For this reason fusion with the alkaline hydrates must never be made in platinum vessels. Platinum very readily forms alloys with metals, particularly with easily reducible ones.

Platinum forms two oxides—platinous (PtO) and platinic (PtO_2). Platinic hydroxide ($Pt(OH)_4$) is easily soluble in dilute acids and in sodium hydroxide. All of its salts are decomposed on ignition, yielding a residue of metal. Platinic chloride at a low red heat is converted into platinous chloride, and this at a higher temperature gives metallic platinum. Cuprous chloride also reduces platinic chloride or potassium platinichloride to the platinous salt.

Platinic Sulphide (*PtS_2*).—H_2S in cold acid or neutral solutions precipitates the sulphide slowly and incompletely, and only after the solution has been kept saturated with the gas for a long time. In hot solutions the precipitate forms much more rapidly.

Platinic sulphide is insoluble in all acids when used alone, but is soluble in aqua regia or chlorine. The alkaline polysulphides in large excess and with the aid of heat dissolve it, but only very slowly. From these solutions it is reprecipitated by acids.

Precipitation by Potassium or Ammonium Salts.—Neutral or slightly acid solutions of platinic chloride if not too dilute are precipitated by potassium or ammonium chloride as yellow crystalline precipitates of potassium or ammonium platinichlorides (K_2PtCl_6 or $(NH_4)_2PtCl_6$).

With dilute solutions it is necessary to evaporate on the water-bath almost to dryness and treat the residue with dilute alcohol.

The potassium precipitate on ignition is decomposed, yielding a residue of metallic platinum and potassium chloride. The ammonia salt leaves only metallic platinum.

Reducing Agents.—Ferrous sulphate after long boiling produces a precipitate of metallic platinum.

Stannous chloride gives no precipitate, but changes the color of the solution to a dark red, due to the reduction of the platinic salt to platinous:

$$PtCl_4 + SnCl_2 = PtCl_2 + SnCl_4.$$

Potassium nitrite gives no immediate precipitate, but after standing for some time a yellow precipitate is thrown down, $K_2Pt(NO_2)_4$.

Oxalic and sulphurous acids do not precipitate platinum solutions even on boiling.

Metallic zinc precipitates platinum very rapidly from its solutions.

SEPARATION OF GOLD AND PLATINUM.

These metals are very easily separated from each other by adding ammonium chloride to a solution of their chlorides, evaporating on the water-bath nearly to dryness, and extracting the residue with alcohol, which dissolves the ammonium aurichloride, leaving the ammonium platinichloride. To the alcoholic solution containing the gold water is added, and the solution evaporated on the water-bath to expel the alcohol. The gold is then precipitated by ferrous sulphate or oxalic acid.

The yellow precipitate containing the platinum on ignition leaves a residue of metallic platinum.

In practical work gold and platinum are seldom met with except in alloys (in ores they are determined by fire-assay). From these they are separated by treatment with acids or fusion with acid potassium sulphate, which leaves the gold and platinum undissolved. Fusion with sodium-potassium carbonate and nitrate reduces gold and platinum compounds to the metallic state.

After removal of the other metals by treatment with acids the gold and platinum are dissolved in aqua regia and then separated from each other, as already given.

When present in solution they will, if not removed by some of the methods given, be found either wholly or partially with the other metals of the sixth group. Owing to the great difficulty with which platinic sulphide dissolves in ammo-

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NOTES TO SCHEME V.

NOTE 1.—The addition of hydrochloric acid should be made with care, for it is very important that the filtrate be acid, yet a large excess of acid is not admissible, since it prevents the complete precipitation of the metals by H_2S. It must also be remembered that bismuth and antimony salts may be precipitated on the addition of hydrochloric acid, and that a moderate excess of dilute acid is necessary to dissolve them. If on washing the precipitate the washings come through turbid, add a few drops of HCl to the wash-water.

If the original solution before the addition of the HCl has an alkaline reaction, it should be remembered that on adding acid to such a solution we may obtain a precipitate of any of those metals whose hydroxides are soluble in alkali. The precipitate in this case, however, will redissolve on the further addition of acid (except lead). In the case of metals of the sixth group dissolved in alkalies or alkaline sulphides the precipitate is insoluble in moderate excess of acid, and it usually shows a characteristic color. If the original solution is alkaline, and hydrochloric acid gives a colored precipitate, insoluble in an excess of the dilute acid, the precipitate should be filtered off, and after washing, digested with $(NH_4)_2S_x$ to dissolve any of the sixth group metals, which are to be tested for in the usual way in the filtrate. The residue insoluble in the $(NH_4)_2S_x$, is dissolved in hot dilute nitric acid and again tested with hydrochloric acid.

NOTE 2.—It is important that all the lead chloride should be washed out before testing for the silver and mercury, as it interferes with the latter tests.

NOTE 3.—Add the ammonia in small portions at a time, otherwise much of the silver may be left in the residue, owing to a reaction between the metallic mercury formed by the action of ammonia on mercurous chloride and the silver chloride whereby metallic silver is precipitated:

$$2Hg + 2AgCl = 2Ag + Hg_2Cl_2.$$

NOTE 4.—The object in boiling out the excess of ammonia is to avoid the formation of much ammonium nitrate, since this salt has some solvent action on silver chloride.

NOTE 5.—Dissolve this residue in as little aqua regia as possible, then evaporate carefully until all free chlorine is expelled, dilute with a little water, and if there is any residue, filter, and test the residue (probably AgCl) for silver. The filtrate is tested for mercury with a few drops of stannous chloride ($SnCl_2$).

NOTE 6.—As stated in Note 1, it is very important that the solution to be precipitated by H_2S should have a proper quantity of free acid (best HCl): if there is not enough present, there is danger of zinc precipitating; and if the solution is too acid, the metals of the fifth and sixth groups are not completely thrown down. It is always a simple matter to determine roughly the quantity of free acid in this solution, by taking a little in a test-tube, and adding solution of sodium carbonate until a permanent precipitate is formed. The amount of sodium carbonate used of course indicates the quantity of free acid. When a solution is found to be strongly acid, it is, as a rule, the best plan to evaporate to small bulk, and then dilute with water. In case bismuth or antimony were present, the addition of water may cause a precipitate; but this can be disregarded, as the H_2S will convert it all into sulphide.

Instead of removing the excess of acid by evaporation, the solution is sometimes largely diluted with water, and then precipitated with H_2S. In cases where only the fifth and sixth groups are to be determined, this plan might be used to advantage, but not when all of the groups have to be tested for. Neutralization of the free acid by alkali is not advisable.

The best method of conducting the precipitation is to pass a rapid current of H_2S gas into the solution until, on shaking, it smells strongly of H_2S. The precipitate of sulphides should be very thoroughly washed with water containing H_2S.

When washed with pure water only, certain sulphides are liable to assume the colloidal condition, and pass through the filter, giving a dark-colored filtrate.

The filtrate from the H_2S precipitate should always be tested, to see if the precipitation has been complete; either by adding to a portion a large excess of H_2S water, or, what amounts to the same thing, pass in H_2S gas, and if this gives no more precipitate, add a large excess of water, and again saturate with the gas. The water is added, to so dilute the free acid present that it will not prevent the complete precipitation of the *metals* as sulphides. Of course, if any precipitate is obtained by these tests, then the whole of the filtrate must be treated in the same way.

Whichever way the filtrate is tested, it should always be heated to 60° or 70° C. for some time, in order to precipitate any arsenic acid that may be present.

NOTE 7.—The treatment of the sulphides with $(NH_4)_2S_x$ is best made by removing the precipitate from the filter-paper, placing it in a small beaker, adding sufficient of the ammonium sulphide to completely cover the precipitate, warming for a few minutes, filtering by decantation, and repeating the treatment of the residue two or three times with small quantities of the $(NH_4)_2S_x$. The final residue must be washed very thoroughly with water containing a few drops of ammonium sulphide, so as to wash out all chlorides; otherwise the subsequent treatment with nitric acid would form aqua regia, and dissolve the mercuric sulphide.

NOTE 8.—The residue at this point is not always black, even when mercury is present, since the mercuric sulphide is sometimes changed by the boiling with nitric acid to the light-colored compound $2HgS,Hg(NO_3)_2$. This is tested in the same way as the black sulphide, by dissolving in chlorine, and precipitating with stannous chloride.

It should be remembered that this residue sometimes contains lead as sulphate, particularly if the nitric acid used was strong. The best way to test for it is on charcoal with the blowpipe. Tin in the form of metastannic acid is also sometimes found here, owing to the treatment of the sulphides with $(NH_4)_2S_x$ having been incomplete.

NOTE 9.—Evaporate the solution carefully, almost to dryness, so as to expel the excess of nitric acid, then before adding sulphuric acid to the whole of it, test a small portion by adding a considerable excess of dilute sulphuric acid, allow to stand a few minutes, and if a precipitate forms, add the acid to the remainder of the solution. If no precipitate forms in the first test, do not add any acid to the rest of the solution, but proceed to test for bismuth with ammonia.

It is advisable to test a few drops of the concentrated solution for silver by diluting with water and adding hydrochloric acid.

NOTE 10.—Success in making this test depends on having very little free hydrochloric acid and a large excess of water.

Another good way to make the test is to dissolve the precipitate on the filter paper in a little dilute hydrochloric acid, allowing the solution to run through into a small porcelain dish, evaporate until only a drop or two of liquid remains, and pour this into a large test tube full of water.

The fact of a precipitate forming on the addition of ammonia in excess is not proof of the presence of bismuth, for if lead or mercury had not been completely removed from the solution they would be precipitated by that reagent.

NOTE 11.—If copper is not present, as shown by the test with ferrocyanide, do not add potassium cyanide to the remainder of the solution, but make it slightly acid with dilute hydrochloric acid, and pass in H_2S gas to precipitate the cadmium.

If the precipitate for cadmium be dark colored, it is best to confirm it on charcoal with the blowpipe. (See Cadmium.)

NOTE 12.—Add only enough acid to make solution slightly acid. An excess of acid might dissolve sulphide of tin.

NOTE 13.—Place the sulphides in a small porcelain dish, add enough concentrated hydrochloric to cover the precipitate, and heat to boiling, adding from time to time a small crystal of potassium chlorate. If antimony or tin sulphides only are present, they will dissolve in the hot hydrochloric alone, so it is always well to boil a few moments before adding any chlorate, for if everything dissolves (except a little sulphur) no arsenic can be present, and no further test for it is necessary.

Continue heating until everything except the separated sulphur has dissolved, and all free chlorine has been expelled.

NOTE 14.—The reagents used in this test should always be tested for arsenic and antimony, as these are impurities frequently met with in hydrochloric and sulphuric acids and in zinc. The surest way to test their purity is to put some of the zinc and acid in a Marsh apparatus, and test the evolved gas for arsenic and antimony by the mirror test on cold porcelain. (See Arsenic and Antimony.)

The solution supposed to contain arsenic and antimony should always be added in small quantities at a time, otherwise the reaction may become so violent as to spoil the test.

NOTE 15.—The silver nitrate is added so as to make sure of some being present, since that added in the first place to the solution may have been all precipitated by the arsenic and antimony.

Very dilute ammonia should be used, and it is best to add it so that it forms a layer over the silver solution. This may be done by pouring it very carefully down the side of the test-tube. At the junction of the two liquids a yellow ring of silver arsenite will be formed if arsenic be present.

NOTE 16.—A small amount of an orange-colored precipitate is sometimes obtained here, due to the presence of a little antimony in the solution.

NOTE 17.—When possible, rinse precipitate off the filter into a test-tube with a little water, add a small piece of tartaric acid, and boil. Then add a few drops of hydrochloric acid and filter.

If the precipitate given by H_2S is not the proper color (orange), it may be easily tested for antimony by dissolving it in a few drops of boiling concentrated hyrochloric, and placing the solution in a platinum capsule with a piece of zinc, when, if antimony is present, the characteristic black stain will make its appearance.

NOTE 18.—The tin in this residue is generally in the form of loose spongy particles, from which the zinc can easily be removed. Antimony. if present, is there as black flakes or powder.

It is best to remove the zinc before dissolving the tin. This is readily done by picking out the hard lumps of zinc with a pair of pincers.

Note 19.—It is always well to test in this residue for antimony, if it has not already been found in precipitate 15.

If the current of hydrogen in the Marsh apparatus has been weak, a large amount of the antimony is often left here in the metallic state.

Note 20.—Another plan for separating these sulphides is as follows: Rinse the precipitate into a beaker, add a lump of ammonium carbonate, and warm gently for a few minutes, filter, and wash.

Residue	Filtrate
SnS_2, Sb_2S_5.	$(NH_4)_3AsS_4 + (NH_4)_3AsO_4$.
Dissolve in hot concentrated hydrochloric acid. Place solution in platinum capsule with a piece of zinc. Antimony, if present, gives the well-known black stain, and the tin is found as a spongy mass. Remove the undissolved zinc, and boil the residue with a little strong hydrochloric acid. The tin dissolves as stannous chloride, and after filtering may be tested with mercuric chloride. A further test for antimony may be made by dissolving the residue, if any, left by hydrochloric acid, in chlorine, and precipitating with H_2S.	Acidify with hydrochloric acid, filter, and wash.
	Ppt.
	As_2S_5.
	Heat with a little concentrated nitric acid unti dissolved. Test a portion of th solution for arsenic aci with ammonium molyb date. Another portion te with magnesia mixture.

This method is not quite exact, as some of the antimony and tin sulphides are liable to go into solution, and a little of the arsenic may be left in the residue. Still it is a rapid method, and for ordinary work sufficiently accurate.

SCIENCE DEPARTMENT
THE STUYVESANT HIGH SCHOOL
345 EAST 15th STREET
NEW YORK CITY

SECTION II.

THE ACIDS.

The detection of the acids cannot be effected by methods similar to those used for the bases. They do not form distinct groups as the metals do, which can be separated from each other by precipitation and filtration.

In almost all cases they are determined by special tests. Although we cannot divide and separate them group from group, still it has been found convenient to classify them to some extent—this classification depending on their deportment with barium chloride and silver nitrate; those acids giving a precipitate with barium chloride in neutral solution forming one division or group, and those precipitated by silver nitrate from solutions acid with nitric acid constituting the second division. Besides these there are two acids (nitric and chloric) that are not precipitated by any reagent, and for this reason are put in a group by themselves.

The classification just given is for the inorganic acids only, and they are the only ones that will be considered in the following pages.

The presence of organic acids can easily be determined by evaporating to dryness and igniting a neutral solution. If present, they leave a carbonaceous residue.

First Group.—Precipitated by barium chloride from neutral solution: Chromic acid (anhydride, CrO_3), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), boric or boracic acid (H_3BO_3), hydrofluoric acid (HF), carbonic acid (CO_2, anhydride), and silicic acid (H_4SiO_4). All these acids, with the exception of hydrofluoric, are precipitated by silver nitrate from neutral solutions.

Second Group.—Precipitated by silver nitrate from solutions acid with nitric acid: Hydrochloric acid (HCl), hydrobromic acid (HBr), hydriodic acid (HI), hydrocyanic acid (HCN or HCy), hydroferrocyanic (H_4FeCy_6), hydroferricyanic ($H_6Fe_2Cy_{12}$), hydrosulphuric acid (H_2S).

Third Group.—Not precipitated by any reagents: Nitric acid (HNO_3) and chloric acid ($HClO_3$).

FIRST GROUP.

PRECIPITATED BY BARIUM CHLORIDE FROM NEUTRAL SOLUTIONS.

CHROMIC ACID (Anhydride, CrO_3).

Chromic acid (H_2CrO_4) has not been obtained in the free state, although many salts corresponding to such an acid are known, some of them beautifully crystalline. The anhydride forms beautiful scarlet crystals, deliquescent, and very soluble in water, imparting to the solution a reddish-yellow color, which is visible in very dilute solutions. On ignition it yields chromic oxide (Cr_2O_3) and oxygen. It acts as a very powerful oxidizing agent, and as a caustic on living tissues. A mixture of chromic anhydride and concentrated sulphuric acid forms an extremely active oxidizing mixture. It is used in the analysis of pig iron to oxidize the graphite to carbonic acid:

$$4CrO_3+6H_2SO_4+3C=2Cr_2(SO_4)_3+3CO_2+6H_2O$$

The chromates are all red or yellow, the color being visible even in very dilute solutions. Those of the first and second group metals, with the exception of barium, are soluble in water; all the others insoluble, or nearly so.

Reduction of Chromic Acid or Chromates to Salts of Chromic Oxide (Cr_2O_3).—Some of the most characteristic reactions of chromic acid depend on its active oxidizing properties, the chromic acid or chromate being at the same time reduced to chromic oxide. The reduction is clearly indicated by the change in color from the red or yellow of the chromate to the bluish-green of the chromic salt. If H_2S be added to an acid solution of a chromate a precipitate of sulphur is formed, and the solution changes in color from red or yellow to bluish green:

$$K_2Cr_2O_7 + 8HCl + 3H_2S = Cr_2Cl_6 + 2KCl + \underset{\smile}{3S} + 7H_2O.$$

This reaction is of special importance, for it is evident that although chromium may be originally present as the acid, the precipitation of the metals with H_2S will always reduce it to chromic salt, and it will consequently be found among the bases. The change in color will, however, surely denote its presence. A means of distinguishing between it and the basic chromium will be given later.

Ammonium sulphide causes the same reduction and then precipitates the chromic salt formed, yielding a precipitate of hydroxide.

Many other substances reduce chromic acid or chromates to chromic salt, such as sulphurous acid (*a*), concentrated hydrochloric acid (*b*), dilute hydrochloric acid and alcohol (*c*), stannous chloride or zinc in acid solution (not nitric) (*d* and *e*), tartaric and oxalic acids, etc.

$$(a)\ K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \\ = Cr_2(SO_4)_3 + K_2SO_4 + H_2O;$$

$$(b)\ K_2Cr_2O_7 + 14HCl \\ = Cr_2Cl_6 + 2KCl + 3\overset{\frown}{Cl}_2 + 7H_2O;$$

$$(c)\ K_2Cr_2O_7 + 9HCl + 4C_2H_5OH \\ = Cr_2Cl_6 + C_2H_5Cl + 3C_2H_4O + 8H_2O + 2KCl;$$

$$(d)\ K_2Cr_2O_7 + 14HCl + 3SnCl_2 \\ = Cr_2Cl_6 + 3SnCl_4 + 2KCl + 7H_2O;$$

$$(e)\ K_2Cr_2O_7 + 3Zn + 14HCl \\ = Cr_2Cl_6 + 2KCl + 3ZnCl_2 + 7H_2O.$$

All these reductions are made evident by the change in color from red or yellow to bluish *green.*

Reactions of Chromates with the Bases.

Barium Chromate (*$BaCrO_4$*). — Barium chloride added to solutions of the chromates gives a yellow precipitate of barium chromate ($BaCrO_4$). The precipitate is soluble in hydrochloric and nitric acids, and decomposed by sulphuric acid. It is nearly insoluble in acetic acid.

$$K_2CrO_4 + BaCl_2 = \underbrace{BaCrO_4} + 2KCl.$$

Lead Chromate (*$PbCrO_4$*).—Soluble chromates added to lead salts give a yellow precipitate of lead chromate, slightly soluble in dilute nitric acid, insoluble in acetic acid and in ammonia. Soluble in sodium or potassium hydrates, from which solutions it is reprecipitated on acidifying with acid (best to use acetic):

$$K_2CrO_4 + Pb(NO_3)_2 = \underbrace{PbCrO_4} + 2KNO_3;$$

$$\underbrace{PbCrO_4} + 4KOH = K_2CrO_4 + K_2PbO_2 + 2H_2O.$$

Silver Chromate.—Normal chromates in neutral solutions of silver salts give a dark-red precipitate of silver chromate (Ag_2CrO_4). In slightly acid solutions the dichromate is precipitated ($Ag_2Cr_2O_7$).

Both precipitates are soluble in nitric acid and in ammonia:

$$K_2CrO_4 + 2AgNO_3 = \underbrace{Ag_2CrO_4} + 2KNO_3.$$

Perchromic Acid ($H_2Cr_2O_8$?).—A very beautiful and delicate test for chromic acid is made by taking a little of a very dilute and acid solution of hydrogen peroxide, adding a small quantity of ether, and then the solution containing the chromic acid or chromate.

The liquid in the tube changes to a beautiful blue color, and if the tube be closed and inverted several times the solution becomes colorless, and the color is now concentrated in the layer of ether. This blue color is probably due to perchromic acid, but the compound is so unstable that its composition has not been satisfactorily determined. The following equation may, perhaps, represent the action that takes place:

$$2H_2CrO_4 + H_2O_2 = H_2Cr_2O_8 + 2H_2O.$$

SULPHURIC ACID (H_2SO_4).

Sulphur when burned forms the oxide SO_2 called sulphurous anhydride, which with water forms sulphurous acid (H_2SO_3)—at least the salts *formed* correspond to an acid of this composition, although the acid itself cannot be isolated, as it at once splits up into sulphurous anhydride (SO_2) and water. This oxide can take up one more atom of oxygen, forming sulphuric anhydride (SO_3), which combines readily with water, yielding sulphuric acid (H_2SO_4).

Sulphuric anhydride when in the solid state is usually in the form of white, silky crystals. These on exposure to the air quickly absorb moisture and become liquid.

Concentrated sulphuric acid is a heavy, oily liquid, colorless and transparent.

Both the anhydride and the acid dissolve in water in all proportions, and the solution is accompanied by the evolution of much heat. Owing to their great affinity for water, the concentrated acid and the anhydride char many kinds of organic matter.

The boiling-point of the acid in 338° C.

The sulphates with few exceptions are colorless.

All of the normal sulphates, with the exception of barium, strontium, calcium, and lead sulphates, are soluble in water.

In alcohol only the ferric sulphate is soluble.

Basic sulphates, which are insoluble in water, are soluble in hydrochloric or nitric acids.

Barium Sulphate.—Barium salts added to a solution containing sulphuric acid or a sulphate give a very finely divided white precipitate of barium sulphate, even from exceedingly dilute solutions. The precipitate is insoluble in water and in dilute acids.

When testing the solubility of this precipitate it should be remembered that concentrated hydrochloric or nitric acids precipitate barium salts. This precipitate, however, is easily soluble in water; so that if the solution be diluted with water there will be no danger of mistaking one precipitate for the other, since the barium sulphate would remain insoluble, whilst the chloride or nitrate would dissolve:

$$H_2SO_4 + BaCl_2 = \underbrace{BaSO_4} + 2HCl.$$

Lead Sulphate ($PbSO_4$).—Sulphuric acid or soluble sulphates give with lead salts a white precipitate of lead sulphate, the properties of which have already been given under lead.

Insoluble Sulphates.—Sulphates insoluble in water and acids may be changed to soluble compounds by fusion with sodium potassium carbonate.

In the fusion the sulphuric acid of the insoluble compound combines with the sodium or potassium carbonate and forms a sulphate soluble in water. The base with which it was combined is changed to carbonate or oxide, insoluble in water:

$$\mathrm{BaSO_4} + \mathrm{Na_2CO_3} = \mathrm{BaCO_3} + \mathrm{Na_2SO_4};$$

$$\mathrm{PbSO_4} + \mathrm{Na_2CO_3} = \mathrm{PbO} + \mathrm{Na_2SO_4} + \overset{\frown}{\mathrm{CO}}_2.$$

If the fused mass be treated with water the sulphate of soda dissolves and can be tested for in the solution, after acidifying with hydrochloric acid, by the addition of barium chloride.

Instead of fusing with the alkaline carbonate, the same result may be obtained, although not so readily, especially with barium sulphate, by boiling with a strong solution of the carbonate. The bases will be changed to carbonates, and the sulphuric acid goes into solution as sodium sulphate.

Blowpipe Test.—If a sulphate be mixed with dry sodium carbonate and fused on charcoal in the reducing flame, it is reduced to sulphide. By placing the fused mass on a piece of bright silver and moistening with water a dark stain of silver sulphide is formed.

It must be remembered, however, that any substance containing sulphur will give the same result, so the test is only conclusive when it is known that all sulphur compounds except sulphate are absent.

Detection of Free Sulphuric Acid.—Free sulphuric acid can be easily detected by adding a very little cane-sugar to the solution, and evaporating to dryness on the water-bath. If any of the acid is present in the free state, a black carbonaceous residue remains, or if the quantity of acid is very small, simply a brown color.

PHOSPHORIC ACID (H_3PO_4).

Common phosphorus is a colorless, transparent solid, insoluble in water, but easily soluble in carbon disulphide.

It melts at 44.3° C., and boils at 290° C.

It oxidizes when exposed to the air at ordinary temperatures, giving off white fumes which have a characteristic odor and are luminous in the dark. When heated in presence of air it ignites very readily, evolving heavy white vapors of the pentoxide, P_2O_5.

Colorless phosphorus is very poisonous, and for *this* reason, as well as on account of its great inflammability, it must be handled with extreme care.

It should always be kept under water, and any pieces required for experiment ought to be cut off while it is still protected in this way.

If phosphorus be heated to 250° C. in a vessel to which air has not free access, it is changed to a red modification, called amorphous phosphorus. This differs from the colorless variety in being less inflammable, is not luminous, is insoluble in carbon disulphide, and is not poisonous.

Phosphoric anhydride or pentoxide (P_2O_5) is a snow-white and very deliquescent solid. With water it forms three different acids. If dissolved in cold water it yields metaphosphoric acid, HPO_3, which on standing gradually changes to pyrophosphoric acid, $H_4P_2O_7$, and finally to orthophosphoric acid, H_3PO_4. The latter acid is also formed by dissolving the pentoxide in boiling water or by boiling a solution containing either the meta- or pyrophosphoric acids:

$$P_2O_5 + H_2O = 2HPO_3;$$

$$P_2O_5 + 2H_2O = H_4P_2O_7;$$

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

Salts of the first two acids are also formed by subjecting orthophosphates containing hydrogen or a volatile base to a high temperature; as, for example,

$$Na(NH_4)HPO_4 - (NH_3 + H_2O) = NaPO_3, \text{ Sodium metaphosphate};$$

$$2MgNH_4PO_4 - (2NH_3 + H_2O) = Mg_2P_2O_7, \text{ Magnesium pyrophosphate.}$$

Compounds of pyro- and metaphosphoric acid are seldom met with, almost all the phosphates in nature and in analysis being salts of the ortho-acid (H_3PO_4). Magnesium pyrophosphate, however, is of importance, since it is the form in which magnesium is generally weighed in analysis; and "phosphorus salt" ($Na(NH_4)HPO_4$), which on fusing into a bead becomes metaphosphate, is a useful blowpipe reagent.

The salts of orthophosphoric acid are all insoluble in water, with the exception of those of the alkalies. In acids their solubility varies: those of the alkaline earths are soluble in hydrochloric, nitric, and acetic acids; ferric and aluminium phosphates are insoluble in acetic but soluble in the mineral acids.

Reactions of Orthophosphoric Acid. Barium Phosphate.—In neutral or alkaline solutions of phosphates barium chloride produces a white precipitate of barium phosphate, easily soluble in acetic, nitric, and hydrochloric acid:

$$\mathrm{Na_2HPO_4 + BaCl_2 = \underbrace{BaHPO_4} + 2NaCl.}$$

Magnesium Phosphate.—The precipitation of phosphates from neutral or alkaline solutions by magnesium salts is very important. It will be remembered that this is the reaction made use of for determining magnesium, and when we have an alkaline solution it affords an equally good test for phosphoric acid. Its use for the detection of phosphates, however, is very limited, owing to the fact that the test has to be made in the presence of ammonia; and since all the phosphates, with the exception of those of the first-group metals, require acid to hold them in solution, it can only be used when we have a phosphate of an alkali metal. Arsenic acid also must be absent, as it too precipitates magnesium salts from alkaline solution.

In neutral solutions magnesium salts give a white precipitate of magnesium hydrogen phosphate ($MgHPO_4$) (*a*), or magnesium phosphate ($Mg_3(PO4)_2$), according to the conditions; but in presence of ammonium chloride and free ammonia a white crystalline precipitate of magnesium ammonium phosphate is formed, even in very dilute solutions(*b*). All of these precipitates are soluble in acetic and mineral acids.

$$(a)\ Na_2HPO_4 + MgCl_2 = \underbrace{MgHPO_4} + 2NaCl.$$

$$(b)\ Na_2HPO_4 + MgCl_2,\ NH_4Cl + NH_4OH$$
$$= \underbrace{MgNH_4PO_4} + 2NaCl + NH_4Cl + H_2O.$$

Silver Phosphate (Ag_3PO_4).—Nitrate of silver gives with neutral solutions of phosphates a yellow precipitate of silver phosphate soluble in nitric acid and ammonia.

$$Na_2HPO_4 + 3AgNO_3 = \underbrace{Ag_3PO_4} + 2NaNO_3 + HNO_3.$$

Ferric Phosphate.—If to an acid solution containing phosphate an excess of sodium acetate be added and then ferric chloride drop by drop, a yellowish-white precipitate of ferric phosphate will be formed. If the addition of the ferric chloride is continued until the solution assumes a reddish tinge, and the solution boiled, all the phosphoric acid will be precipitated in combination with the iron, and the excess of iron present will be thrown down as basic acetate. This reaction is of great importance, as it enables us to separate phosphoric acid from its combinations with the alkaline earths.

$$\begin{aligned} &2Na_2HPO_4 + Fe_2Cl_6 + 2NaC_2H_3O_2 \\ &\qquad = \underbrace{2FePO_4}_{} + 6NaCl + 2HC_2H_3O_2, \end{aligned}$$

$$\begin{aligned} \text{or } &2MgHPO_4 + Fe_2Cl_6 + 2NaC_2H_3O_2 \\ &\qquad = \underbrace{2FePO_4}_{} + 2MgCl_2 + 2HC_2H_3O_2 + 2NaCl. \end{aligned}$$

Ammonium Phosphomolybdate.—Of all the tests for phosphoric acid this is the most valuable, as it enables us to precipitate phosphoric acid not only from acid solutions, but from solutions containing almost all the metals.

If to a solution of ammonium molybdate be added a few drops of a neutral or acid solution containing a phosphate, a yellow precipitate of ammonium phosphomolybdate($(NH_4)_3PO_4, 12\,MoO_3$) is formed. The formation of the precipitate is hastened by heating the solution gently, *not above* 70° C. Care must be taken in making this test always to have the ammonium molybdate present in considerable excess, otherwise the precipitate may not be thrown down. Arsenic and silicic acids, if present in the substance to be tested, must previously be removed, as they also are precipitated by ammonium molybdate, although not so readily as the phosphate. The solution best suited for the reaction is one slightly acid with nitric acid.

The precipitate of phosphomolybdate after being washed with a solution of ammonium nitrate may be dissolved in ammonium hydrate and the phosphoric acid precipitated with "magnesia mixture" ($MgCl_2$, $NH_4Cl + NH_4OH$).

BORIC OR BORACIC ACID (H_3BO_3).

Boron is infusible and non-volatile, and when heated in the air burns to boric anhydride (B_2O_3). This is a colorless glass fusible at a red heat, and soluble in water and alcohol. On evaporating these solutions boric acid volatilizes with the water or alcohol. For this reason acid solutions of borate must always be neutralized before concentration.

Boric anhydride forms with water metaboric acid (HBO_2) and orthoboric acid (H_3BO_3), also several other hydrates of more complex composition. The borates of the alkalies are soluble in water, the others insoluble. They are not decomposed on ignition. Although boric acid is a very weak one when in solution, yet in the dry state it acts very powerfully, driving out the strongest acids from their combinations, by simply fusing them with the acid or its anhydride.

Although boric acid or borates form insoluble precipitates with many metals, yet none of them are of much analytical importance. With barium salts borates give a white precipitate soluble in acids and in ammonium salts. Silver nitrate in concentrated solutions gives a white precipitate of silver borate, in dilute solutions a precipitate of silver oxide. Both are soluble in nitric acid and ammonia.

Turmeric Test.—A very delicate test for boric acid is made by dipping a piece of turmeric paper into a solution of a borate made slightly acid with hydrochloric acid; the paper is then dried on the water-bath, when it assumes a characteristic red tint. If the paper colored in this way be moistened with alkali the color changes to black or dark green, but is restored again by addition of a little dilute hydrochloric acid.

In making this test much free hydrochloric acid must not be present, as it gives a brownish-black color with turmeric paper. Ferric chloride also gives a brownish-red color, and for this reason should be removed before making the test.

Flame Tests.—If alcohol be poured over dry boric acid or a borate, in the latter case concentrated sulphuric acid being added to liberate the boric acid, and the alcohol lighted, the flame will be colored green by the boric acid. Frequently the color is only seen on the edges of the flame. The test is made more delicate by blowing out the flame after allowing it to burn for a few moments, and then relighting it, when the edges of the flame will be tinged green—only momentarily if the quantity of boracic acid is small.

Chlorides and copper salts interfere with this test, as they give the same color to the flame. Copper may be removed by precipitating with H_2S and the chlorides by silver sulphate.

The same coloration may be obtained by making a borate into a paste with a drop or two of concentrated sulphuric acid, heating the mixture gently in the Bunsen flame on the loop of a platinum wire, so as to expel excess of sulphuric acid, and then dipping the bead into glycerine. It is then lighted by holding in the flame for a moment, and on removing from the same it continues to burn with a green flame.

FLUORINE (F) AND HYDROFLUORIC ACID (HF).

Fluorine is exceedingly difficult to prepare in the free state, owing to the ease with which it combines with almost all substances to form fluorides.

It decomposes water instantly, forming hydrofluoric acid and ozone. It also attacks glass or other silicates readily, forming silicon fluoride (SiF_4).

Fluorine is always found in nature as fluoride, chiefly as fluor-spar (CaF_2); it is also contained in cryolite ($NaAlF_4$), and in small amount in apatite ($Ca_3(PO_4)_2$).

Hydrofluoric Acid.—In the anhydrous state this is a colorless, fuming liquid, boiling at 20° C. and readily soluble in water. It differs from all other acids in its property of dissolving silica, and for this reason is especially valuable in the analysis of silicates. All metals with the exception of gold and platinum are soluble in it with evolution of hydrogen.

The fluorides of the alkalies, and a few others are soluble in water. Strong sulphuric acid liberates hydrofluoric acid from fluorides.

Barium Fluoride.—Barium chloride gives with aqueous solutions of hydrofluoric acid or of fluorides a white precipitate of barium fluoride, very insoluble in water, and difficultly soluble in cold hydrochloric or nitric acid.

From these acid solutions it is not reprecipitated on the addition of ammonia, owing to the solubility of barium fluoride in ammonia salts:

$$2NaF + BaCl_2 = \underbrace{BaF_2} + 2NaCl.$$

Calcium Fluoride.—Calcium chloride added to aqueous solutions of hydrofluoric acid or fluorides gives a gelatinous precipitate of calcium fluoride of much the same solubility as barium fluoride. Addition of ammonia helps the precipitation. Ammonium salts prevent it.

Etching Test.—The most characteristic test for hydrofluoric acid depends on its property of combining with the silica of silicates, with the formation of volatile silicon fluoride. If a finely pulverized fluoride is placed in a lead or platinum dish, and made into a thin paste with concentrated sulphuric acid, and then gently warmed, hydrofluoric acid is evolved. A watch-glass covered with a thin coating of wax or paraffin, in which some letter or figure has been traced with a hard wooden point, is placed closely over the dish, and the latter gently warmed for half an hour. (Care must be taken not to let the heat get high enough to melt the wax, for if this happens, of course, the etching is prevented.) At the end of this time the glass is taken off and the wax removed by warming, and wiping with a cloth; the figure made in the wax will be found etched into the glass.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2\overbrace{HF};$$

$$SiO_2 \text{ (of the glass)} + 4HF = \overbrace{SiF_4} + 2H_2O$$

The presence of silica or a silicate in the fluoride to be tested prevents or impairs this reaction, since the hydrofluoric acid liberated combines with that in preference to the silica of the glass. In this case the test is made as follows:

Place the finely pulverized fluoride containing silica or silicate in a *dry* test-tube. Add concentrated sulphuric acid in sufficient quantity to cover the fluoride and heat gently.

If now a drop of water in a loop of platinum be held in the mouth of the tube the drop will become opaque and solid, due to the silicon fluoride being decomposed by the water into hydrofluosilicic acid (H_2SiF_6) and silica (SiO_2).

Instead of using the drop of water the evolved gas may be passed over into water by fitting the test-tube with a perforated cork and bent-glass tube. When making the test in this way care must be taken that the end of the tube that dips into the water does not become choked by the separated silica, as this might cause an explosion; also, do not allow the water to draw back into the tube containing the sulphuric acid for the same reason. The water into which the gas has been passed will be found to have an acid reaction, due to the hydrofluosilicic acid formed. The first reactions are the same as in the previous test, but the silicon fluoride formed in this last one is decomposed by the water as follows:

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + \underbrace{H_4SiO_4}.$$

Silicates not decomposable by sulphuric acid should first be fused with sodium potassium carbonate, the fusion dissolved in water and filtered, the filtrate made *very slightly* acid with hydrochloric acid, and boiled to expel carbonic acid. After cooling it is made alkaline with ammonia and calcium chloride added, and any precipitate that forms is dried and tested by one of the methods just given.

SILICIC ACID (H_4SiO_4,H_2SiO_3).

Silicon forms but one oxide, SiO_2, called silica or silicic anhydride. This oxide is found very abundantly in the mineral kingdom, as quartz, rock crystal, etc., and in the form of silicate it forms the greater part of the earth's crust. It is insoluble in water and acids, with the exception of hydrofluoric.

Under certain conditions it unites with water to form hydrates or acids as H_4SiO_4,H_2SiO_3. Amorphous silica and the hydrated acids dissolve in hot sodium or potassium hydrates, and in their carbonates, forming silicates. Also somewhat soluble in ammonia, but not in ammonia carbonate.

Fusion with alkali or alkaline carbonate yields a silicate soluble in water.

Silica is not affected by heat even at extremely high temperatures.

Of the silicates only those of the alkalies are soluble in water. Many of those insoluble in water are decomposed by acids, while others resist their action entirely, and can only be gotten into solution by previous fusion with alkaline carbonate, whereby the silicate is decomposed and the silica unites with the alkali to form a soluble silicate.

Silicic Acid.—Solutions of alkaline silicates are easily decomposed by all acids.

If excess of hydrochloric acid be added to a solution of sodium or potassium silicate, no precipitate forms at first, but after standing for some time the whole mass solidifies as a transparent jelly. If, however, the acid be added drop by drop, silicic acid is precipitated in a gelatinous form.

By adding hydrochloric or nitric acid in excess to a solution of a silicate and evaporating the solution to complete dryness (110°–115° C.), the silicic acid separates as anhydride (SiO_2). By treating the dry residue with hydrochloric acid and water the insoluble silica is left as a residue. The last reaction is very generally made use of for separating silica from its combinations. With silicates decomposed by acid, all that is necessary is to first boil the very finely pulverized mineral with an excess of strong hydrochloric acid, during which operation the geater part of the silicic acid separates, generally as a gelatinous precipitate, sometimes as a pulverulent one.

As soon as the mineral is completely decomposed the mixture is evaporated to dryness and heated in the air-bath, with occasional stirring, until no odor of acid is perceptible. The dry residue is then moistened with a little concentrated hydrochloric acid, a small quantity of water added, and the mixture heated until everything except the silica has gone into solution. The silica is then filtered off, and on drying appears as a white gritty powder.

In the case of silicates not decomposable by acid, the mineral, as already stated, must first be fused in a platinum crucible with a mixture of four or five parts of sodium potassium carbonate. (The fusion should be continued until the mass is perfectly liquid, and no more gas is given off.) The fused mass is then treated with water, and, without previous filtration, sufficient hydrochloric or nitric acid is added to make the solution acid; the mixture is then evaporated to dryness and the silica separated as in the previous method.

When it is required to test for the alkalies in a silicate that is not decomposed by acid, the fusion method just given is, of course, not admissible. In such cases the mineral is fused with barium or calcium oxides *instead* of sodium or potassium carbonate, and the silica separated in the same way as if the carbonates had been used.

Silicon Fluoride.—Hydrofluoric acid as gas, or in strong aqueous solution, converts silica into silicon fluoride, SiF_4 (see hydrofluoric acid); in dilute solution it dissolves silica with formation of hydrofluosilicic acid:

$$SiO_2 + 6HF = H_2SiF_6 + 2H_2O.$$

Silicates when treated with hydrofluoric acid yield silicofluorides (*a*), but if sulphuric acid be present the silicofluoride is decomposed into sulphate, silicon fluoride, and hydrofluoric acid.

$$(a)\ CaSiO_3 + 6HF = CaSiF_6 + 3H_2O;$$

$$(b)\ CaSiF_6 + H_2SO_4 = CaSO_4 + \overbrace{SiF_4} + \overbrace{2HF}.$$

Ammonium or calcium fluoride (of course free from silica) may be used in place of hydrofluoric acid. To a mixture of three or four parts of the fluoride and one of the silicate, in a platinum crucible or dish, concentrated sulphuric acid is added and the mixture warmed. If a drop of water in the loop of a platinum wire be now held over the dish, the water will become cloudy or opaque, due to the separated silicic acid (see hydrofluoric acid).

This method of decomposing a silicate may be used to advantage when it is required to test for the alkalies in silicates undecomposable by other acids.

Blowpipe Test.—If silica or a silicate be fused in a salt of phosphorus bead ($NaPO_3$), the bases with which the silica was combined dissolve, while the silica floats about in the bead in the same form as the piece of mineral added, yielding the so-called silica skeleton. This test is not altogether reliable, as certain silicates such as the zeolites dissolve completely, while some other substances containing no silica, as apatite, are not acted on.

CARBONIC ACID (Anhydride, CO_2).

Carbon is found in many different forms—such as the diamond (crystallized carbon), which is exceedingly hard and transparent; as graphite, which is soft, opaque, and black; all the different kinds of coal, charcoal, etc. It is insoluble in acids, and infusible. Some varieties are easily combustible; others, as the diamond and graphite, are burnt with difficulty.

When burned with an excess of oxygen or air it yields carbon dioxide or anhydride (CO_2)

(commonly called carbonic acid); if the carbon is in excess the product is carbon monoxide (CO).

Carbonic Anhydride (CO_2).—Carbon dioxide or anhydride is at ordinary temperatures and pressures a colorless and almost odorless gas of high specific gravity (1.52). At 0° C. and a pressure of 36 atmospheres it condenses to a liquid, which if allowed to evaporate rapidly causes a fall in temperature to −80° C., and a portion of the liquid solidifies as a snow-white mass.

The gaseous dioxide is somewhat soluble in water, one volume of cold water dissolving about one volume of the gas. Air containing carbon dioxide even in comparatively small amount is unfit for respiration, and many a fatal accident has been caused by inhaling it. The dreaded "after-damp" of coal-mines consists largely of this gas. It will not support combustion, a lighted candle being instantly extinguished if plunged into a vessel filled with it. This may be made use of as a rough test to determine whether the air in any confined space, as a shaft or well, contains much carbon dioxide.

If on lowering a lighted candle into a shaft the light is extinguished, it is proof that the air contains the gas in considerable quantity. A mixture of air and gas containing only 25% of CO_2 will extinguish a burning candle.

Carbon dioxide is a very weak acid. It turns blue litmus red, but on drying the blue color reappears. It forms carbonates with many of the metals, and of these only the carbonates of the alkalies are soluble in water. All carbonates, however, are soluble in acids, even in very weak ones, except in hydrosulphuric and hydrocyanic.

The carbonates are very widely distributed in nature, as limestones, marbles, chalk, dolomite, etc., also in many mineral springs, and in almost all waters to a greater or less extent. The atmosphere also contains a certain amount of carbon dioxide, which although small in amount (0.05% to 0.1%) is a very important constituent, since it supplies plants with their carbon, their leaves with the aid of sunlight being able to decompose the carbon dioxide, assimilating the carbon and liberating oxygen.

As already stated, carbonates are soluble in almost all acids, most of them dissolving even in the cold; a few, however, require heat (magnesite, siderite, etc.). The decomposition is accompanied by *effervescence*, caused by the escaping carbon dioxide (*a*). The acid used to decompose the carbonate should always be added in excess so as to prevent the formation of any acid carbonate (*b*), since carbonic acid forms acid carbonates with a few of the metals, particularly those of the alkalies ($KHCO_3$, $NaHCO_3$, etc.).

To prove that the gas evolved is really carbon dioxide it is passed into a solution of lime or baryta water, or a glass rod that has been dipped in baryta-water is held in the test-tube in contact with the gas. If carbon dioxide is present the lime or baryta water becomes turbid, owing to the formation of a precipitate of carbonate (*c*).

If an excess of the gas is passed into the solution the precipitate will dissolve, but on boiling it again precipitates, the excess of the dioxide being driven off by the heat.

$$(a)\ Na_2CO_3 + 2HCl = \overbrace{CO_2} + 2NaCl + H_2O;$$

$$(b)\ Na_2CO_3 + HCl = NaHCO_3 + NaCl;$$

$$(c)\ Ca(OH)_2 + CO_2 = \underbrace{CaCO_3} + H_2O.$$

Barium or Calcium Carbonate.—With solutions of the normal carbonates barium and calcium *chlorides* give white precipitates of carbonate.

In dilute solutions of acid carbonates the precipitate only forms on boiling.

With solutions of carbonic acid no precipitate is formed unless the solution be neutralized:

$$Na_2CO_3 + BaCl_2 = \underbrace{BaCO_3}_{} + 2NaCl.$$

Lead Carbonate.—An ammoniacal solution of lead acetate or an aqueous solution of lead chloride gives in solutions of normal or acid carbonates a white precipitate of carbonate. All neutral solutions of lead salts are precipitated by the normal carbonates.

ACIDS OF THE SECOND GROUP.

The characteristics of this group are the precipitation by silver nitrate from solutions acid with nitric acid, and the fact that barium chloride does not precipitate them.

The acids are *hydrochloric*, *hydrobromic*, *hydriodic*, *hydrocyanic*, *hydroferrocyanic*, *hydroferricyanic*, and *hydrosulphuric*.

HYDROCHLORIC ACID (HCl).

Chlorine is a heavy, yellowish-green gas, possessing a characteristic odor, and is extremely irritating to the respiratory organs. It is soluble in water, forming a solution of a faint yellowish-green color. This solution on exposure to light decomposes into hydrochloric acid and oxygen (*a*).

Chlorine, both as a gas and in solution, acts as a strong bleaching agent, destroying many vegetable colors, and in solution is a very powerful oxidizing agent. It combines freely with the alkaline hydrates, forming hypochlorite (*b*) in cold solution and chlorate in hot (*c*).

(*a*) $2H_2O + 2Cl_2 = 4HCl + O_2$;

(*b*) $2KOH + Cl_2 = KClO + KCl + H_2O$;

(*c*) $6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O$.

Hydrochloric acid at ordinary temperatures is a colorless, suffocating gas, fuming in moist air, and very soluble in water. Concentrated solutions lose a considerable amount of the gas on heating. The acid is easily formed from chlorides by heating them with sulphuric acid. It is made commercially from common salt in this way:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The normal chlorides are all easily soluble in water, with the exception of silver, lead, mercurous and cuprous chlorides. Bismuth and antimony chlorides require the presence of some free acid to hold them in solution.

Chlorine occurs in nature principally as sodium chloride (common salt), either in the form of rock salt or, dissolved in water, as sea-water. It is also found to some extent as potassium and magnesium chlorides (Stassfurth deposits).

Silver Chloride.—Hydrochloric acid and almost all chlorides, even in exceedingly weak solutions, give with silver nitrate a white precipitate of silver chloride, which changes to a violet or black color on exposure to light. For solubilities, etc., of precipitate, see silver chloride, under head of Silver.

Mercurous and Lead Chlorides.—Solutions of either mercurous or lead salts are precipitated by hydrochloric acid or soluble chlorides, as already given under those metals.

Evolution of Chlorine.—If hydrochloric acid be heated with manganese dioxide or lead dioxide, chlorine is evolved (*a*), which is easily recognized by its yellowish-green color, its odor, and bleaching action on vegetable colors. If a piece of moist litmus paper is held in the fumes the color will be destroyed. In the case of chlorides some strong sulphuric acid must be added as well as the dioxide (*b*).

Chlorides heated with manganese or lead dioxides and acetic acid do not evolve chlorine.

(*a*) $MnO_2 + 4HCl = \overset{\frown}{Cl_2} + MnCl_2 + 2H_2O$.

(*b*) $2NaCl + MnO_2 + 3H_2SO_4$

$= \overset{\frown}{Cl_2} + 2NaHSO_4 + MnSO_4 + 2H_2O.$

Free hydrochloric acid alone or in presence of chlorides is easily detected by simply heating the solution with manganese dioxide, when chlorine is evolved as in reaction (*a*).

Chromic Oxychloride (CrO_2Cl_2).—If a dry chloride be mixed with potassium dichromate and placed in a small flask or test-tube, and some concentrated sulphuric acid added and the mixture gently heated, chromic oxychloride or chromyl chloride (also called chloro-chromic acid) will be liberated as a reddish-brown gas that condenses on cooling to a red liquid (*a*). If the flask or test-tube be fitted with a delivery-tube, and the gas passed into ammonia, a yellow solution of ammonium chromate is obtained (*b*). On acidifying this solution with acetic acid, and adding a drop or two of lead acetate, a yellow precipitate of lead chromate is formed.

(*a*) $$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 = 2CrO_2Cl_2 + 2KHSO_4 + 4NaHSO_4 + 3H_2O;$$

(*b*) $$CrO_2Cl_2 + 4NH_4OH = (NH_4)_2CrO_4 + 2NH_4Cl + 2H_2O.$$

This test is of particular value for determining chlorides in the presence of bromides, the latter forming no corresponding compound, but liberating bromine instead:

$$6KBr + K_2Cr_2O_7 + 11H_2SO_4$$
$$= 3Br_2 + 8KHSO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

The bromine when passed into ammonia gives a colorless solution. Iodides with dichromate and sulphuric acid act in the same way as bromides.

Insoluble Chlorides.—For the detection of chlorine in the chlorides insoluble in water and nitric acid, they should be fused with sodium potassium carbonate, the fusion extracted with water, and the chloride tested for in the filtrate.

Blowpipe Test.—If a salt of phosphorus bead be saturated with cupric oxide, and then a small quantity of any substance containing a chloride be added, and the substance heated in the reducing flame, the flame will be colored blue.

HYDROBROMIC ACID (HBr).

Bromine is a heavy, dark-red liquid which boils at 63° C. Even at ordinary temperatures it volatilizes freely, giving off heavy red fumes that are exceedingly irritating.

It is more soluble in water than chlorine (a saturated solution contains about 3% of bromine), and easily soluble in ether, chloroform, or carbon disulphide. If an aqueous solution of bromine be shaken with one of the substances just mentioned they will extract the bromine from the water solution, the latter becoming colorless, and the ether or disulphide appears of a red or yellow color. Bromine, like chlorine, is a strong bleaching and oxidizing agent, and the reactions are similar.

Hydrobromic acid at ordinary temperatures is a colorless gas, very soluble in water.

The acid itself or its aqueous solution decomposes slowly in presence of air, bromine being liberated, which colors the solution red or yellow.

Bromides are only found in small quantities. They are contained in sea-water, and in many salt springs.

In chemical properties the bromides resemble the corresponding chlorides very closely.

Silver Bromide.—As already stated under the reactions for silver, bromides or hydrobromic acid precipitate silver salts as bromide, insoluble in nitric acid. For further properties of the precipitate, see silver bromide, under head of "Silver."

Liberation of Free Bromine.—Hydrobromic acid and all bromides except silver bromide are decomposed by heating with nitric acid, bromine being set free:

$$6KBr + 8HNO_3 = 3Br_2 + 6KNO_3 + 2\overline{NO} + 4H_2O.$$

Chlorine either as gas or in solution decomposes bromides, liberating bromine.

Alkaline hypochlorites as sodium hypochlorite ($NaClO$) effect the same reaction if added to solutions slightly acid with hydrochloric acid. The addition of either reagent must be made with care, as an excess of it converts the bromine into colorless bromine chloride. If before liberating the bromine a few drops of carbon disulphide or chloroform be added to the solution, and then the chlorine water or hypochlorite and the mixture be gently shaken, the bromine is all taken up by the disulphide or chloroform, which now shows a red or yellow color.

It is always advisable to test the reagents by making a blank test (*i. e.*, making a test in the same way, except that pure water is substituted for the solution to be tested for bromine), to see if they give any color with the carbon disulphide.
ld any color appear, either new reagents
used or the color obtained in the blank
be compared with that given by the
er examination.

Bromides with manganese or lead dioxides and sulphuric acid give the same reactions as chlorides, the only difference being that a more dilute solution of sulphuric acid can be used than with the latter.

With manganese dioxide and acetic acid bromides are not decomposed, but with lead dioxide and acetic acid bromine is liberated (a distinction from chlorides).

Action on Starch.—If a bromide be mixed with manganese dioxide and sulphuric acid in a small beaker, and the latter covered with a watch-glass, having a strip of paper attached to the under side which has been moistened with starch-paste and sprinkled with starch powder, on heating the mixture gently the liberated bromine colors the starch-paste yellow.

Insoluble Bromides.—Bromides insoluble in nitric acid are fused with sodium potassium carbonate, and the fused mass treated in the same way as for chlorides.

Blowpipe Test.—Bromides when heated in reducing flame in a salt of phosphorus bead which has been saturated with cupric give a blue flame inclining to green.

HYDRIODIC ACID (HI).

Iodine generally occurs in the form of black crystalline scales having a decided lustre. It fuses at 115° C., and boils at 200° C. (Stas), with evolution of violet fumes which condense in a crystalline form. It is only very slightly soluble in water, but dissolves easily in alcohol, ether, chloroform, carbon disulphide, and in aqueous solution of iodides. The solutions in chloroform and carbon disulphide are violet, the others brown or reddish-brown.

Certain reducing agents as thiosulphates (*a*) and sulphites (*b*), dissolve free iodine, yielding colorless solutions.

$2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$ (sodium tetrathionate);

$2I + Na_2SO_3 + H_2O = 2HI + Na_2SO_4$.

Starch-paste, even with minute traces of iodine, gives a beautiful blue color.

Iodine has only very weak bleaching properties; the action on litmus and other vegetable colors is very slow. It stains the skin brown.

Hydriodic acid is a colorless gas at ordinary temperatures, and is very soluble in water, giving a colorless solution. This solution soon turns brown, owing to the gradual decomposition of the hydriodic acid, iodine being liberated and dissolving in the remaining acid.

Iodides.—Iodides in many ways correspond to the chlorides and bromides, but more of them are insoluble in water, and generally these insoluble compounds are soluble in excess of the iodide, forming double iodides.

Silver Iodide.—Soluble iodides give with solution of silver nitrate a yellow precipitate of silver iodide. The precipitate is soluble in excess of the iodide, forming a double iodide ($KI.AgI$). It is insoluble in dilute nitric acid, and almost insoluble in dilute ammonia. Soluble in thiosulphate and potassium cyanide.

Mercurous and Lead Iodides.—These have already been described under their respective metals.

Cuprous Iodide.—Sulphate of copper precipitates soluble iodides as white cuprous iodide, free iodine being liberated at the same time (*a*). In presence of reducing agents, as ferrous sulphate (*b*) or sulphurous acid (*c*), no free iodine is formed. Addition of ammonia assists the precipitation.

$$(a)\ 4KI + 2CuSO_4 = \underbrace{Cu_2I_2} + I_2 + 2K_2SO_4\,;$$

$$(b)\ 2KI + 2CuSO_4 + 2FeSO_4 = \underbrace{Cu_2I_2} + Fe_2(SO_4)_3 + K_2SO_4\,;$$

$$(c)\ 4KI + 2CuSO_4 + SO_2 + 2H_2O = \underbrace{Cu_2I_2} + 2K_2SO_4 + H_2SO_4 + 2HI.$$

Chlorides and bromides are not precipitated by these reagents.

Liberation of Free Iodine.—The most delicate and characteristic tests for iodides depend on the liberation of free iodine, the presence of the iodine being then made evident by suitable means. Iodides are decomposed by many different reagents, iodine being set free in the reaction, such as concentrated sulphuric or nitric acids, nitrous acid even in dilute solution, chlorine, bromine, etc.

If a solution containing an iodide, even in extremely minute quantity, be acidified with a few drops of dilute sulphuric acid, then some starch-paste* added, and finally a couple of drops of potassium nitrite, the solution will become blue, or if only traces of iodine are present, a reddish-violet. The test should always be made in a cold solution, as heat destroys the color. Chlorine may also be used for this test, but is not so well suited for it, as an excess bleaches the color.

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* Starch-paste is made by mixing one part of starch with about 100 parts of cold water and then heating until a solution is obtained that is almost clear. This solution should be freshly prepared for each experiment.

Another very delicate test for iodine is made by adding to the solution to be tested a few drops of chloroform or carbon disulphide, and then very carefully, drop at a time, a solution of chlorine water or a hypochlorite; on shaking the mixture the liberated iodine dissolves in the chloroform or carbon disulphide with a beautiful violet or purple color.

Other reagents that liberate iodine may be used for this test, such as nitrite and sulphuric acid. When chlorine or hypochlorite is used the reagent must be added carefully, since an excess of the reagent forms colorless iodine chloride.

If iodides are heated with ferric sulphate or chloride, iodine is set free:

$$2KI + Fe_2(SO_4)_3 = \overset{\sim}{\overline{I}_2} + 2FeSO_4 + K_2SO_4.$$

This may be used as a separation from chlorides and bromides.

With manganese or lead dioxides and dilute sulphuric or acetic acids, and with potassium dichromate and dilute sulphuric acids, iodine is set free, and, unless in very small quantity, may be recognized by its violet color.

Insoluble Iodides.—Iodides insoluble in acid are fused with sodium potassium carbonate and the fusion treated as already given for bromides or chlorides.

Blowpipe Test.—Iodides when fused in the reducing flame in a salt of phosphorus bead saturated with cupric oxide give a green flame.

HYDROCYANIC ACID (HCN or HCy).

Cyanogen (C_2N_2) is a colorless gas, having a characteristic odor, and when lighted burns with a violet flame. It may be prepared by the ignition of silver or mercuric cyanide.

Hydrocyanic acid is a colorless, volatile liquid, boiling at 27° C., and having a very characteristic odor, resembling that of bitter almonds.

It is soluble in water and alcohol in all proportions, but these solutions soon undergo decomposition if concentrated; in dilute solution it is more stable.

Hydrocyanic or prussic acid is one of the most poisonous substances known. The soluble cyanides are also exceedingly poisonous, and great care must be taken in handling them. The cyanides of the alkalies and alkaline earths are soluble in water, and the solutions obtained are decomposed by acids, even by carbonic acid. All cyanides are decomposed by evaporating with concentrated sulphuric acid.

Potassium and sodium cyanides are valuable reducing agents. They can be fused without decomposition if air be excluded; but when fused with substances capable of yielding oxygen, such as metallic oxides, they reduce these and are converted into cyanate (*a*). Sulphides are reduced in the same way, yielding thiocyanate (*b*):

$$SnO_2 + 2KCN = Sn + 2KCNO;$$
$$PbS + KCN = Pb + KCNS.$$

The cyanides of the heavy metals are all decomposed on ignition, yielding either the metal or a carbide of the metal.

Cyanides combine with the bases to form different classes of compounds—as the simple cyanides (as KCN), double cyanides (as $AgCN,KCN$), and compound cyanides (as K_4FeCy_6 or $K_6Co_2Cy_{12}$).

The simple cyanides (*a*) have a great tendency to combine and form soluble double cyanides (*b*), from which solutions they are reprecipitated on acidifying with acid (*c*):

$$(a)\ Co(NO_3)_2 + 2KCy = \underbrace{CoCy_2} + 2KNO_3;$$
$$(b)\ CoCy_2 + 4KCy = CoCy_2,4KCy;$$
$$(c)\ CoCy_2,4KCy + 4HCl = \underbrace{CoCy_3} + 4KCl + 4\overbrace{HCy}.$$

In a compound cyanide the cyanogen is combined with the metal in such a way that the two act as if they were a simple element (such a combination is called a compound radical), and the metal no longer acts as it does in simple solutions; for example, the iron in potassium ferrocyanide no longer gives the ordinary reactions of that metal, and, indeed, we use this very solution as a reagent to test for iron.

These compound cyanides on addition of dilute acids give no precipitate of a cyanide, as the double cyanides do. On evaporation with strong sulphuric acid, however, they are decomposed into hydrocyanic acid and metallic sulphate, which remains as a residue.

Simple Cyanides.—Silver nitrate added to a solution of hydrocyanic acid or a soluble cyanide gives a white precipitate of silver cyanide (*a*) which is easily soluble in potassium cyanide, forming double cyanide (*b*); it is also soluble in ammonia; insoluble in dilute nitric acid. On boiling with strong hydrochloric acid it is decomposed into silver chloride and hydrocyanic acid:

$$(a)\quad KCN + AgNO_3 = \underbrace{AgCN} + KNO_3;$$
$$(b)\quad AgCN + KCN = AgCN,KCN.$$

Silver cyanide on ignition is decomposed, yielding metallic silver, cyanogen, and some silver paracyanide.

Formation of Ferrocyanide.—If to a solution containing hydrocyanic acid or a cyanide a mixture of ferrous and ferric (a drop or two only of the ferric is required) salt be added, then sufficient sodium or potassium hydrate to make the solution alkaline, and the mixture gently heated, the cyanide is changed to ferrocyanide, and on acidifying the solution a blue precipitate of Prussian blue is obtained:

$$6KCN + FeSO_4 = K_4Fe(CN)_6 + K_2SO_4.$$

Formation of Thiocyanogen (*Sulphocyanogen*).—Another very delicate test for hydrocyanic acid or cyanides is made by adding to the solution a few drops of ammonia and a little strong ammonium sulphide (polysulphide) and evaporating to dryness at a gentle heat (best on water-bath). The residue, which now contains thiocyanate, is made acid with hydrochloric acid and a drop of ferric chloride added, when the well-known blood-red color of ferric thiocyanate appears:

$$KCN + (NH_4)_2S_x = KCNS + (NH_4)_2S_{x-1}.$$

The evaporation to dryness decomposes the excess of ammonium sulphide, so that the residue is free from that compound. When making this test it is well to add the hydrochloric acid in moderate excess, otherwise acetates, phosphates, etc., if present, will interfere with the reaction.

Hydroferrocyanic Acid ($H_4Fe(CN)_6$).—This acid is a colorless, crystalline solid, easily soluble in water. The ferrocyanides of the alkalies and alkaline earths are soluble in water, most of the others insoluble.

The insoluble compounds are easily brought into solution by boiling with sodium or potassium hydrates, the metal with which they were combined, if its hydrate is insoluble in the alkali, being left as a residue.

$$Fe_4(Fe(CN)_6)_3 + 12KOH$$
$$= \underbrace{2Fe_2(OH)_6} + 3K_4Fe(CN)_6.$$

If the metallic hydroxide is soluble in alkali (as $Zn(OH)_2$, $Pb(OH)_2$, etc.) it also goes into solution, and must be precipitated from the alkaline liquid by H_2S. All ferrocyanides, as already stated, are decomposed by evaporation with strong sulphuric acid. Fusion with sodium or potassium nitrate effects the same result.

Silver Ferrocyanide.—Nitrate of silver gives with ferrocyanides a white precipitate of silver ferrocyanide ($Ag_4Fe(CN)_6$), insoluble in nitric acid and ammonia, soluble in potassium cyanide.

The most characteristic test for ferrocyanides is made by adding to the slightly acid solution a few drops of a ferric salt, when, if ferrocyanides are present, a deep-blue precipitate (Prussian blue) will be formed.

Cupric salts also give a characteristic red precipitate.

Hydroferricyanic Acid ($H_6Fe_2(CN)_{12}$).—Many of the ferricyanides are soluble in water, and all are decomposed in the same manner as the ferrocyanides.

Nitrate of silver gives an orange-colored precipitate of silver ferricyanide ($Ag_6Fe_2(CN)_{12}$), insoluble in nitric acid, soluble in ammonia, and potassium cyanide.

Ferric salts give no precipitate, but ferrous give a deep-blue precipitate of ferrous ferricyanide ($Fe_3Fe_2(CN)_{12}$). This test is characteristic and exceedingly delicate.

Thiocyanic Acid (*Hydrosulphocyanic*).—Thiocyanic acid or thiocyanates (sulphocyanides) are readily detected by the blood-red color given by ferric salts in hydrochloric-acid solution.

HYDROSULPHURIC ACID (H_2S).

Sulphur at common temperatures is a solid body, generally of a yellow color, but precipitated sulphur is white. It is insoluble in water and alcohol, soluble in benzol, petroleum, and carbon disulphide, the latter substance being its best solvent. Amorphous sulphur is generally insoluble in the disulphide. There is also a colloidal modification that is soluble in water. Sulphur fuses at 115° C. and boils at 444° C.

When heated in the air it burns with a bluish flame to sulphur dioxide, the latter being recognized by its well-known and characteristic odor. Strong oxidizing agents, as concentrated nitric acid, aqua regia, hydrochloric acid, and potassium chlorate, etc., with the aid of heat, dissolve sulphur *gradually*, forming sulphuric acid. Potassium and sodium hydrates dissolve it, on heating, to a yellow liquid containing sulphide and thiosulphate. Sulphur is often found in the free state in connection with deposits of gypsum and rock salt, and in the vicinity of volcanic craters. Sicily furnishes a large proportion of the world's supply.

Free sulphur in a substance can generally be easily detected by igniting it in the air, when it burns with a blue flame and the characteristic odor of sulphur dioxide. The test is best made by heating the mixture in a glass tube open at both ends, the tube being held in a slanting position and the heat applied to the part where the substance rests.

If heated in a tube closed at one end the sulphur volatilizes as yellowish-brown vapors that condense in the upper, cold portion of the tube to brown drops, turning yellow on cooling.

Hydrosulphuric Acid or Hydrogen Sulphide at common temperatures and pressure is a colorless, poisonous gas, having the odor of rotten eggs. It is easily inflammable, burning to sulphur dioxide and water.

It is soluble in water, but the solution is not stable. For this reason, when used as a precipitating agent it should be freshly made. It is generally obtained by the action of acids on metallic sulphides (usually ferrous sulphide).

$$FeS + 2HCl = FeCl_2 + \overbrace{H_2S}.$$

Sulphides.—The sulphides of the heavy metals are found very widely distributed in nature, and form many of the most valuable ores. The sulphides of the alkalies and alkaline earths are the only ones soluble in water. These and the sulphides of iron, zinc, and manganese are decomposed by cold dilute mineral acids, with evolution of hydrosulphuric acid.

Of the other sulphides, some are soluble in hot, strong hydrochloric acid; others require nitric acid or aqua regia (*i.e.*, chlorine).

When nitric acid or mixtures yielding chlorine are used, hydrosulphuric acid is not liberated, but sulphur is set free (*a* and *b*), and frequently the action goes further, the sulphur being oxidized to sulphuric acid (*c* and *d*):

$$(a)\ 3Ag_2S + 8HNO_3 = 6AgNO_3 + \underbrace{3S} + 4H_2O + 2\overbrace{NO};$$

$$(b)\ HgS + Cl_2 = HgCl_2 + \underbrace{S};$$

$$(c)\ 3PbS + 8HNO_3(\text{hot and conc.}) = 3PbSO_4 + 8\overbrace{NO} + 4H_2O;$$

(*d*) $S + 3Cl_2 + 4H_2O = H_2SO_4 + 6HCl.$

Detection of Hydrosulphuric Acid.—When in the gaseous state or in solution this acid is easily recognized by its odor, or by bringing the acid in contact with lead or silver salts, when black precipitates of sulphide are formed. A convenient way of making the test is to hold in the gas a piece of filter-paper that has been moistened with lead acetate and then made alkaline by the addition of a drop or two of ammonia; if H_2S is present, even in minute quantity, the paper shows a brown or black lustrous film of lead sulphide. Sulphides decomposed by hydrochloric acid are tested in the same manner, by placing them in a test-tube with the acid and heating, a piece of paper moistened with lead acetate and ammonia being held at the mouth of the tube.

Sulphides decomposed with difficulty by hydrochloric acid, if treated in a small flask or test-tube with hydrochloric acid and finely divided iron free from sulphur (ferrum alcoholisatum), evolve H_2S along with the hydrogen liberated by the action of the acid on the iron. If the flask or tube has been loosely corked, and a piece of acetate of lead paper fastened to the under side of the cork, the paper will be turned black or brown by the sulphide. Realgar, orpiment, and molybdenite are not decomposed.

To detect sulphide in presence of free alkali or alkaline carbonate, a solution of lead hydroxide in sodium or potassium hydrate (made by adding the alkaline hydrate in excess to a soluble lead salt) is added, when even a trace of sulphide gives a black or brown precipitate; or if the amount is very minute, simply a brown color (1 part of lead in 1,000,000 parts of water may be detected in this way).

Sodium nitroprusside

$$(Na_4Fe_2(CN)_{10}(NO)_2,2H_2O)$$

added to alkaline solutions is also a very delicate test for sulphides, giving a reddish-violet tint to the solution.

Sulphides insoluble in acids should be fused with sodium or potassium hydrate in a silver or nickel crucible. A soluble sulphide of the alkali is formed that can be tested by any of the ods just given, or, what is simpler, the fused placed on a piece of bright silver and vith water, when the silver is turned lphide present.

Oxidation to Sulphate. If a sulphide be fused with sodium potassium carbonate and an oxidizing agent, as sodium nitrate or potassium chlorate, the sulphide is oxidized to sulphate. The fused mass is then digested with water and filtered, and the filtrate tested for sulphuric acid. This test is, of course, only conclusive in the absence of sulphates and all other substances containing sulphur (except sulphides), for all on fusion in this way yield sulphates.

Blowpipe Test.—If a sulphide be heated in a glass tube open at both ends, in the same way as given for free sulphur, sulphur dioxide will be given off, and may be recognized by its odor. Also, if heated in oxidizing flame of the blowpipe, sulphides yield sulphur dioxide.

SCIENCE DEPARTMENT
THE STUYVESANT HIGH SCHOOL
345 EAST 15th STREET
NEW YORK CITY

THIRD GROUP OF ACIDS.

Acids which are not precipitated by either barium chloride or silver nitrate—viz., nitric acid and chloric acid.

The chief characteristic of this group is that all the nitrates and chlorates are soluble in water, with the exception of a few basic nitrates.

NITRIC ACID (HNO_3).

Nitrogen combines in five different proportions with oxygen—viz., N_2O,—N_2O_2 or NO,—N_2O_3,—N_2O_4 or NO_2. The N_2O,N_2O_3 and N_2O_5 unite with water to form the acids—hyponitrous (HNO), nitrous (HNO_2), and nitric acid (HNO_3).

Nitric acid is the only one of common occurrence, so we will only consider its reactions.

The pentoxide (N_2O_5) is a colorless substance, crystallizing in six-sided prisms, which melts at

30° C. It dissolves in water, with evolution of much heat, forming nitric acid:

$$N_2O_5 + H_2O = 2HNO_3.$$

Nitric acid is a colorless (when free from lower oxides of nitrogen), fuming liquid, very corrosive, and acting powerfully on organic tissues. It boils at 86° C., and its specific gravity is 1.52. It is a strong oxidizing agent, and is a solvent for many metals, in the latter case generally giving off nitric oxide (NO).

Nascent hydrogen in alkaline solution reduces nitric acid to ammonia:

$$KNO_3 + 8H = KOH + NH_4OH + H_2O.$$

On ignition all nitrates are decomposed, leaving a residue of oxide of the metal.

Commercially, nitric acid is made by heating sodium nitrate (Chili saltpetre) with strong sulphuric acid:

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

Since nitric acid forms no insoluble compounds with any of the metals, we are obliged to make use of other reactions for its detection. Its oxidation reactions afford an easy means of recognizing it.

Action on Copper.—If a nitrate be heated with metallic copper and concentrated sulphuric acid (the latter is added to liberate the nitric acid) in a test-tube, the tube becomes filled with reddish-brown fumes of nitrogen peroxide, formed by the oxidation of the nitric oxide:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2\widetilde{NO} + 4H_2O;$$

$$2NO + O_2 = 2NO_2 \text{ (reddish-brown fumes).}$$

Action on Ferrous Salts.—If a solution of nitrate is mixed with an equal volume of concentrated sulphuric acid, *and after the mixture has been cooled* a little ferrous sulphate be poured very carefully down the side of the tube, so that the two solutions do not mix, a brown ring will form at the junction of the two liquids. In making this test it is advisable to have the solutions concentrated. On heating, the brown color disappears:

$$\begin{aligned}&2KNO_3 + 4H_2SO_4 + 10FeSO_4\\&\quad = \underset{\text{(Brown ring)}}{2(FeSO_4)_2NO} + 3Fe_2(SO_4)_3 + K_2SO_4 + 4H_2O.\end{aligned}$$

It will be seen from the equation that a part of the ferrous salt is oxidized, and that another portion combines with the nitric oxide liberated by the reaction to form the brown compound $(FeSO_4)_2NO$. It may perhaps make the action plainer to write the equation in two stages, thus:

$$2KNO_3 + 6FeSO_4 + 4H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + K_2SO_4 + 4H_2O;$$

$$4FeSO_4 + 2NO = 2(FeSO_4)_2NO.$$

Action on Indigo.—A little hydrochloric acid is boiled in a test-tube for a few moments, then a drop or two of indigo in sulphuric acid is added, and the solution again boiled; the solution will remain blue if the hydrochloric acid was free from chlorine. If a solution containing nitric acid or a nitrate is now added, and the solution again boiled, the blue color disappears. The action is due to the liberation of chlorine, which reacts on the indigo. For this reason, any substance yielding chlorine (as chlorate) will give the same reaction. In a negative way the test is very useful, for although the bleaching of the solution is not conclusive for nitrates, still if the color is not destroyed we know that nitrates (also chlorates) are not present.

Action on Phenol.—A test that is well suited to the detection of nitrates when present only in minute quantities (as in well-water, etc.) is made by adding two or three drops of a mixture of one part phenol (carbolic acid), four parts of concentrated sulphuric acid, and two parts of water to a solid nitrate. A reddish-brown color is produced, which changes to yellow on the addition of a few drops of ammonia. The color is due to the formation of a nitro compound with the phenol. ($C_6H_2(NO_2)_3OH$, picric acid.)

When it is desired to test a solution for nitrate in this way the solution, which must be neutral or alkaline, is evaporated to dryness in a porcelain dish and the mixture of phenol, etc., added to the residue. Chlorates, if present, must be removed by ignition before making this test, as they give much the same color.

Nitrates cause deflagration if heated to a dull red with charcoal or organic matter, such as paper. The deflagration is caused by the oxidation of the carbon by the oxygen of the nitrate.

Free nitric acid may be detected by adding to the solution a few quill-cuttings and evaporating to dryness in a porcelain dish or beaker on the water-bath.

If any free nitric acid is present the quills will be turned yellow.

CHLORIC ACID ($HClO_3$).

Chlorine forms four acids with oxygen—viz., hypochlorous acid ($HClO$), chlorous acid ($HClO_2$), chloric acid ($HClO_3$), and perchloric acid ($HClO_4$). Hypochlorous and chloric acids are frequently met with, the first in the form of bleaching-powder, also as Javelle water ($NaClO$), the latter as potassium chlorate.

Hypochlorites act as strong bleaching agents, especially in acid solutions, due to the liberation of chlorine.

Solutions of hypochlorites are decomposed on boiling into chloride and chlorate.

Hypochlorites may be detected by their bleaching action on litmus paper, even in alkaline solutions, and by shaking their solutions with mercury the latter is changed to the yellow or red oxide. Chlorine under the same conditions gives mercurous chloride, white, and chlorates in neutral or alkaline solution do not attack mercury. With manganese salts hypochlorites give a brownish-black precipitate of hydrated manganese dioxide, and with silver nitrate they give a precipitate of silver chloride.

The chlorates are all soluble in water. On ignition they yield oxygen, or, in some cases, oxygen and chlorine; in the first case the residue left is a chloride, in the latter an oxide. This action is employed in the production of oxygen from potassium chlorate:

$$2KClO_3 = 2KCl + 3O_2.$$

Heated with organic matter, the chlorates cause deflagration acting much more strongly than the nitrates. A mixture of potassium chlorate and nitric acid forms a very powerful oxidizing agent.

Hydrochloric acid decomposes chlorates, yielding chlorine and oxides of chlorine, the action varying with the conditions. If the chlorate present is not in too small quantity, the test-tube in which the experiment is made is filled with a yellowish-green gas of a very peculiar and disagreeable odor, and the solution as well becomes yellow. Solution of indigo is quickly bleached by it.

Sulphuric acid also decomposes chlorates into perchloric acid and chlorine tetroxide:

$$6KClO_3 + 3H_2SO_4$$
$$= 2Cl_2O_4 + 2HClO_4 + 3K_2SO_4 + 2H_2O.$$

If a few drops of concentrated sulphuric acid *are placed* in a small evaporating-dish, and a *very* *small* quantity of chlorate added to it, the sulphuric acid assumes an intense yellow color, due to the chlorine tetroxide.

No heat should be used in this test, and only a small amount of the chlorate, otherwise a dangerous explosion may result.

If to the yellow solution just mentioned a drop of an aqueous solution of aniline sulphate be added, and then a few drops of water, a deep-blue color is produced (distinctive from nitric acid).

Indigo in Presence of Sulphite.—If a solution containing chlorate be colored light-blue with a drop or two of indigo in sulphuric acid, the solution made slightly acid with sulphuric acid, and sodium sulphite added drop at a time, the blue color of the indigo is at once destroyed, due to the sulphurous acid reducing the chloric acid and liberating chlorine or oxides of chlorine.

SOLUBILITIES.

1 Name of Salt.	2 Soluble in Water.	3 Soluble or Decomposed by Acids.	4 Insoluble in Water and Acids.
Carbonates	Alkaline carbonates	All	
Sulphates	All sulphates except those in 4	All except those given in 4	$BaSO_4$, $SrSO_4$, $CaSO_4$, $PbSO_4$
Sulphites	Alkaline sulphites and acid sulphites of alkaline earths	All sulphites are decomposed by acids, yielding (SO_2)	
Sulphides	Sulphides of the alkalies and alkaline earths	All; some by HCl, H_2S evol.; others by HNO_3 or aq. reg. S. separating	
Nitrates	All except some basic nitrates	All	
Nitrites	All		
Chlorides	All except those given in 4	All except those given in 4	$AgCl$, $PbCl_2$, Hg_2Cl_2 (Hg_2Cl_2 sol. in HNO_3 or Cl)
Chlorates	All		
Hypochlorites	All		
Iodides	All except PbI_2, HgI_2, BiI_3, Cu_2I_2 and those given in 4.	All except those in 4	AgI, Hg_2I_2, decomposed by Cl
Fluorides	Those of the alkalies and a few others: AgF, HgF_2	All decomposed by strong H_2SO_4 with few exceptions	
Phosphates (Ortho)	Those of the alkalies	All	
Silicates	Potassic and sodic silicates (not native)	Many are decomposed by acids separating H_4SiO_4	Many native silicates (decomposed by HF)
Acetates	All normal	All	
Oxalates	Those of the alkalies and Cr and Sn^{iv} (Mg and Fe^{iv} sparingly)	All	
Tartrates	Normal alkaline tartrates	All	
Citrates	Alkaline citrates	All	
Arsenites and Arsenates	Those of the alkalies	All	
Chromates	Those of the alkalies and Sr, Ca, Mg, Zn, Fe^{iv}, Cu	All, with a few exceptions	

DETECTION OF THE ACIDS.

We have now become acquainted with the most important of the individual reactions of the acids, and the next thing in order is to determine some plan for recognizing them either when alone or mixed with others.

The reactions occurring on the addition of hydrochloric and hydrosulphuric acids in the separation of the bases should always be carefully noted, as the presence of certain acids will be revealed on the addition of these reagents.

If the addition of hydrochloric acid causes an evolution of gas, one or all of the following acids may be present—carbonic, sulphurous, or hydrosulphuric acids. The first is indicated by being odorless and giving a white precipitate with lime or baryta water; the others, by their odor and the action of hydrosulphuric acid on acetate-of-lead paper. Hydrocyanic acid, if present, would also be liberated at this point, and might be recognized by its odor and by confirmatory tests. If the original substance is a solid the same remarks apply to the operation of dissolving it in acids.

The color of the original solution and the action of hydrosulphuric acid show whether chromic acid is present or not. If the solution is red or yellow at first, and after addition of the hydrosulphuric acid changes to a bluish green, chromic acid is present.

It is not possible to make any scheme for the separation of the acids, similar to those used for the bases, but in the one given on the following pages I have endeavored to systematize the separations as much as possible.

SCHEME.—ACIDS.

Boil the solution containing the acids, with excess of Na_2CO_3; filter hot. (Note 1.)

PRECIPITATE A.

Contains bases and perhaps silicates, phosphates, and fluorides.

Divide into two parts.

PART 1°.	PART 2°.
Acidify with HNO_3, and evaporate to dryness. Take up the residue with HNO_3 and H_2O; filter and wash.	Acidify with $HC_2H_3O_2$, and filter.

RESIDUE 1°.	FILTRATE 1°.	RESIDUE 2°.	FILTRATE 2°.
A white, gritty powder = SiO_2. Test with metaphosphate bead.	Add $(NH_4)_6Mo_7O_{24}$ a yellow crystalline ppt., = H_3PO_4.	If no SiO_2 has been found in residue 1°, treat residue 2° with H_2SO_4 (conc.) in a Pb or Pt dish, and see if fumes will etch glass; if they do = HF. Should SiO_2 have been found in residue 1°, treat 2° according to method given for fluorides in presence of silica.	Reject.

FILTRATE A.

Contains the acids.

Divide into two unequal parts.

<table>
<tr><th colspan="2">PART 1° (¾ of A).</th><th rowspan="3">PART 2° (¼ of A.)
Test a portion for $HClO_3$ by evaporation to dryness and adding a few drops of concentrated sulphuric acid. The acid becomes yellow if chloric acid is present.
Evaporate another portion to small bulk, cool and acidify with conc. H_2SO_4, and test for HNO_3 with $FeSO_4$.
Brown ring = HNO_3.
$HClO_3$, HBr, HI, and H_2CrO_4 impede this reaction, and should be removed. (Note 4.)</th></tr>
<tr><td colspan="2">Add HNO_3 to *faintly* acid reaction; then NH_4OH until slightly alkaline, and boil until all free NH_4OH is driven off. Divide into two parts. (Note 2.)</td></tr>
<tr><td>PART 1^a.
Take a small portion of this neutral solution, and add $BaCl_2$. A white ppt. = acids of Group 1. To this ppt. add HCl; all dissolve except $BaSO_4$; proves H_2SO_4.</td><td>PART 2^a.
Take a small portion of this neutral solution, add $AgNO_3$, and then acidify with HNO_3. Ppt. = acids of the 2d Group. Note the color of the ppt. before and after adding HNO_3. (Note 3.)</td></tr>
</table>

SCHEME.—*Concluded.*

If Group 1° has been found by test on part 1a, take the remainder of this solution and divide into four parts:

1°.	2°.	3°.	4°.
Acidify with HCl, and test for H_3BO_3 with turmeric paper. A red color = H_3BO_3. (Note 5.) Evaporate the same solution to dryness, and take up residue with a little HCl and water; a white insol. residue = SiO_2. (Note 6.)	Add $CaCl_2$ and a little NH_4OH; filter ppt. if any (Note 7); dry, and if SiO_2 has not been found in 2° test for HF by etching test. If SiO_2 has been found, then test as given for hydrofluoric acid in presence of silica.	Acidify with HNO_3, add $(NH_4)_6Mo_7O_{24}$. a yellow ppt. = H_3PO_4. If As_2O_5 has been found in the test for bases, it should be removed by acidifying with HCl, passing in H_2S gas, and filtering before testing for H_3PO_4. (Note 8.)	If H_2CrO_4 is present, the solution will be yellow. Confirm by acidifying with $HC_2H_3O_2$, and adding $Pb(C_2H_3O_2)_2$, a yellow ppt. = $PbCrO_4$. (Note 9.)

H_2CO_3. Test the original solution with HCl; if effervescence, pass the gas into lime-water. A white ppt., soluble in $HC_2H_3O_2$, with effervescence proves H_2CO_3.

If 2d Group has been found to be present by test of Part 2^a, test remainder of solution for acids of this Group as follows: Divide into four parts.

1.	2.	3.	4.
Add a little CS_2, and then a few drops of HCl, then NaClO very carefully; the I is set free, and colors CS_2 purple: add more NaClO very carefully, and finally the I color disappears, and the Br is then liberated and colors CS_2 brown. (Note 10.)	Acidify with HCl, and test with $FeSO_4$, a blue ppt. = $H_6(FeCy_6)_2$. The $FeSO_4$ solution must be recently made.	Acidify with HCl and add Fe_2Cl_6: a blue ppt. = H_4FeCy_6.	Acidify slightly with H_2SO_4, and if HCy is present it is known by its peculiar odor. Care should be taken not to inhale this gas. If H_4FeCy_6, or $H_6(FeCy_6)_2$, has been found in 2 and 3, test for HCy as given in note 11.

HCl.	H_2S.
When HI, HBr, H_4FeCy_6, $H_6Fe_2Cy_{12}$ and HCy have not been found, a white curdy ppt. on addition of $AgNO_3$, insoluble in HNO_3, and soluble in NH_4OH = HCl. HCl may also be tested for by means of H_2SO_4 and MnO_2. If HI, HBr, HCy, H_4FeCy_6, and $H_6Fe_2Cy_{12}$ are present, see Note 12 for detection of HCl.	If present, will be found on acidifying the sodium carbonate solution with acid, when H_2S will be given off, and will turn paper moistened with $Pb(C_2H_3O_2)_2$ black. H_2S is usually found in testing for the bases, as it is liberated when dissolving the original substance. (Note 13.)

NOTE 1. — Since the presence of the heavy metals interferes with many of the tests for acids, it is always best to remove them before beginning the analysis. If the substance under examination is a solution, or a solid that is easily soluble in water or acids, they are precipitated by adding to the solution or solid substance a slight excess of sodium carbonate, heating to boiling, and filtering. The acids, with the exception of those precipitated from acid solutions on neutralization (phosphates, etc.), will be in the filtrate as soda salts. This and the residue are tested as given in the scheme.

Another way of obtaining the solution for analysis is, if the substance is a solid, to extract it thoroughly with boiling water and filter.

The filtrate is boiled with a slight excess of sodium carbonate and filtered, and the filtrate tested for acids according to the scheme. The precipitate contains only the bases, and may be rejected. The residue left after extracting the original substance with water is dried and fused in a platinum crucible, if no reducible metals are present, with about four parts of sodium potassium carbonate; the fusion is boiled with water until completely disintegrated, and filtered.

The filtrate is tested in the same way as that obtained by boiling the original substance with the carbonate. If phosphoric acid is not found in the filtrate the residue, or a portion of it, should be dissolved in nitric acid and tested for that acid, as phosphates of the alkaline earths and alumina are not completely decomposed by fusion in this way.

NOTE 2.—Care must be taken to add only enough nitric acid to make the solution slightly acid; it should then be boiled to expel carbonic acid before adding the ammonia. A precipitate sometimes forms at this point (bases soluble in excess of hot sodium carbonate) which should be filtered off.

If much nitric acid is used the subsequent addition of ammonia will form a considerable quantity of ammonium nitrate, which interferes with the test for borates, fluorides, etc.

NOTE 3.—The color of the silver precipitate often indicates the presence of certain acids. For example, if the precipitate is yellow in the neutral solution and changes to white on the addition of nitric acid, this would show the probable presence of phosphoric acid (or arsenious), as well as the presence of acids of the second group. Acids of the latter group giving strongly colored precipitates could not be present (iodides, sulphides, and ferricyanides) if the insoluble portion of the precipitate was white.

NOTE 4.—The test for nitric acid should be deferred until it has been determined if any of these acids are present.

Chloric acid, if present, is removed by evaporating a portion of the alkaline solution to dryness and then igniting it. The residue is dissolved in very little water and tested for nitrate with sulphuric acid and ferrous sulphate. Chromates (indicated by their yellow color) are removed by making the solution slightly acid with sulphuric acid and adding sodium sulphite; the sulphurous acid liberated reduces the chromate to chromium sulphate, which is then precipitated by ammonia, and the filtrate after concentration tested for nitric acid. Hydriodic and hydrobromic acids are removed by precipitation with silver sulphate. (This is readily made by dissolving a silver coin in a little hot concentrated sulphuric acid and after cooling diluting with water.)

NOTE 5.—Remember, in making this test, that the solution must be acid with hydrochloric, but not strongly so.

NOTE 6.—Silica is not generally met with except in minerals, and if the mineral is one decomposable by acid (except hydrofluoric) it is readily found by evaporating the acid mixture to dryness with frequent stirring, at a temperature not exceeding 110°–115° C.

The thoroughly dried mass (which should give no odor of acid) is moistened with a little concentrated hydrochloric acid (if silver or lead are present use nitric acid), some water added, and the mixture boiled for some time. On filtering, the silica will be left as a white, gritty powder. Silicates not decomposed by acids are fused with sodium potassium carbonate, the fusion digested with water, then, without filtering, acidified with hydrochloric or nitric acid and evaporated to dryness, and treated as just given for decomposable silicates.

NOTE 7.—Of course, other acids besides hydrofluoric will give a precipitate at this point (phosphoric, sulphuric, etc.), so the mere fact of a precipitate forming is no proof of hydrofluoric acid. It is well to try its solubility in acetic acid; if soluble, no fluoride is present, and no further test is necessary. In the case of minerals decomposable by sulphuric acid, the test may be made to advantage directly on the finely pulverized substance.

· NOTE 8.—If arsenic acid is present care must be taken to remove it completely by passing H_2S into the hot solution (70° C.) for at least half an hour. The solution should only be slightly acid with nitric acid, since the latter in strong solution decomposes the H_2S. Boil out the H_2S thoroughly before adding the molybdate.

Phosphates, unless present in very minute quantity, may be tested for with "magnesia mixture" ($MgCl_2 + NH_4Cl + NH_4OH$) instead of the molybdate. In this case the arsenic, if present, must be removed, as before, by acidifying (but with HCl) and precipitating with H_2S. The filtrate is then made strongly alkaline with ammonia and the magnesia mixture added.

NOTE 9.—When chromates are present in a mixture, as already stated, they are reduced by H_2S when precipitating the metals, and chromium will then be found among the bases as well as with the acids, although it may only be present in the acid form. In such cases, in order to determine if basic chromium is present, it should be tested for in precipitate A where it will have been left by the treatment with sodium carbonate.

NOTE 10.—The hypochlorite should be added only a drop at a time at first and a weak solution used, for if the iodine is present in small quantity any excess of the hypochlorite would destroy the color. When a large amount of iodine is present, and the carbon disulphide becomes very dark in color, instead of adding more hypochlorite to remove the color it is a better plan to filter the solution through a wet filter; the disulphide, with its dissolved iodine, remains on the paper, and to the filtrate is added fresh carbon disulphide, and the test proceeded with as before. For traces of iodine it would be better to use the starch test.

Cyanides, if present, should be removed before testing, as they interfere with the liberation of the iodine.

For method of doing this, see Note 12.

NOTE 11.—Unless the odor of the hydrocyanic acid is so decided as to be unmistakable, it is better to make the test with ferrous and ferric salt, obtaining the precipitate of Prussian blue.

Or the test with alkaline polysulphide can be used, forming thiocyanate.

In the presence of ferro or ferri cyanides these tests cannot be used. The simplest method of separation in such cases is to add an excess of hydrogen sodium carbonate (bicarbonate) to the solution in a flask fitted with a cork and bent delivery-tube (or better, connected with a condenser), and boil, passing the vapors over into a solution of potassium hydrate. The heating should be continued until the liquid in the flask has nearly all distilled over. The hydrocyanic acid of the cyanide is set free in the reaction and passes over with the steam into the alkali, forming potassium cyanide, on which any of the usual tests for cyanide can be made.

NOTE 12.—The presence of cyanides and ferro- and ferricyanides interferes with the usual test for hydrochloric, hydrobromic, and hydriodic acids, so they must be removed before these acids can be tested for. This is done by precipitating them all as silver salts, filtering, drying, and igniting the precipitate. The cyanogen compounds are all destroyed by this treatment, while the iodide, bromide, and chloride of silver are unchanged. The ignited residue is then fused with sodium potassium carbonate, and the fusion extracted with water and filtered. The filtrate contains the acids as sodium iodide, bromide, and chloride.

Another simple way of decomposing the fused silver salts is to cover them with a little water, add a few drops of sulphuric acid and a piece of zinc, and allow to stand for some time. The solution will contain the acids as zinc iodide, bromide, and chloride, and the residue metallic silver.

$$2AgCl + Zn = 2\underbrace{Ag} + ZnCl_2.$$

Chlorides cannot be tested for in the presence of iodides and bromides by the ordinary methods, and some special method must be adopted. There are several different ways of accomplishing it, one of the simplest of which is the following: Make the solution slightly acid with sulphuric acid, add a concentrated solution of ferric sulphate (ammonium ferric sulphate is a convenient form in which to use it), and boil; the iodine is liberated and carried off with the steam. As soon as no more iodine is set free (indicated by absence of violet fumes, or by test with paper moistened with starch-paste giving no blue color) solution of potassium permanganate is added and the solution again boiled. If the color of the permanganate disappears, more is to be added, and in fficient quantity to give a violet or purple color to the solution that does not disappear quickly, even on boiling.

The permanganate decomposes the bromide, which is evolved as free bromine, and brown oxide of manganese precipitates. The solution is filtered, and the remaining permanganate decomposed by adding a few drops of alcohol, warming, and filtering. Silver nitrate is added to the filtrate, giving, if chlorides are present, a white, curdy precipitate of silver chloride.

Another method of detecting chlorides in the presence of iodides and bromides is to add to the neutral solution lead dioxide and acetic acid and boil until no more iodine or bromine is evolved and the solution becomes colorless.

Filter and wash the precipitate with hot water, and test in the filtrate for chlorides with silver nitrate.

NOTE 13.—When there is any doubt as to the presence of sulphide the surest plan is to fuse the finely divided substance with sodium or potassium hydrate in a silver or nickel crucible and test the fused mass on bright silver. (See hydrosulphuric acid.)

SECTION III.

COMPLETE ANALYSIS, INCLUDING THE METALS AND ACIDS OF ALL THE GROUPS.

Having completed our study of the individual reactions of the different bases and acids as well as the separation and detection of the members of each group when present together in solution, all that now remains to be accomplished is to connect these different group-separations into one connected method that will be applicable in almost all cases that may arise.

Before proceeding further it will be well to call attention to the fact that success as an analyst will depend on several things. Rapidity in work can only be attained by neatness and an intelligent use of time. Lack of neatness and order not only cause the loss of much valuable time, but they are also fruitful sources of error. The student should endeavor to make use of every moment, and for this reason should accustom himself to carry on several operations at the same time. For instance, while filtering a group-precipitate he can test the first few drops of the filtrate to see if the precipitation has been complete, and, if so, he can then determine if any of the metals of the succeeding group are present. He then knows in just what manner to treat the filtrate when it is ready—whether to add the reagents for the next group, or, if his tests have shown that it is not present, he can go on to the precipitation of the remaining groups. Besides making these tests, he will very likely have had time to investigate some other precipitate that has already been filtered and washed. Another point of special importance is to know exactly under what conditions each precipitation should be made, and every one should make it a rule, which should be rigidly adhered to, *never to add any reagent until he knows why it is used, and what it is expected to do.* No one will ever be a good and intelligent analyst who adds a reagent simply because his book tells him to do so. He must know the reason why, and if he does not, he should go no further until he does know.

After a precipitate has been obtained, it is very important in most cases that it should be thoroughly washed, and the thoroughness of the washing should be determined by a confirmatory test. For instance, test the washings with silver nitrate when washing out a solution containing chlorides. Never, because you are in a hurry, slight this important part of your analysis.

Every student should bear in mind when making an analysis that he has two objects in view. One, of course, is to determine what the constituents of the substance are; and the other, which is of equal or even greater importance at this stage of his course, is to gain an intelligent understanding of the methods used.

Let us return now to a study of what is necessary in order to make a complete analysis of any mixture. In the first place, the substance to be examined, if not already in the liquid form, must be gotten into solution. Frequently this is a very simple operation, as, for example, when the material is soluble in water or acids; but in some cases it is more difficult, as in the case of a substance insoluble in acids, and requiring fusion to decompose it, such as barium sulphate and many silicates.

Before attempting to dissolve any substance (other than alloys) it should always be pulverized and gotten into the finest powder possible; the finer it is, the more rapidly will it go into solution, or be decomposed by fusion if the latter proves necessary.

It is well at this point, before proceeding to get the material into solution, to make a preliminary examination on charcoal and in the glass tube, as much valuable information is often gained in this way without the expenditure of much time or labor.

PRELIMINARY EXAMINATION.

TEST A.—Heat a portion gently with oxidizing flame upon charcoal.

Sb.—White pulverulent volatile coat.

The compound often continues to form in dense white fumes after cessation of blast. The coating disappears before reducing flame, tingeing it a pale yellow-green.

As.—White very volatile crystalline coat.

The coat disappears before reducing flame, tingeing it pale blue, and evolving a characteristic garlic odor.

TEST B.—Heat a portion *gently* with the reducing flame on charcoal, and note results. Then add some sodium carbonate and heat *strongly* with the reducing flame for three or four minutes.

As.—Garlic odor and a faint white volatile coat.

Cd.—Dark-brown volatile coat, sometimes shading to greenish yellow, and usually surrounded by a variegated coloration resembling the colors of peacock feathers.

Zn.—White not easily volatile coat, yellow when hot.

Sn.—White non-volatile coat close to assay, and usually small in amount.

White coats may form from Pb, Bi, or alkalis; yellow coats from Pb or Bi; brown or red coats from Cu or Mo; and the ash of the coal may be white or red. If any coat forms, examine it for Zn and Sn by moistening it with cobalt solution and blowing a strong blue flame on the substance. The coating turns green if Zn or Sn are present. The coatings from other elements will not prevent the cobalt coloration.

TEST C.—Mix a portion of the substance with more than an equal volume of bismuth flux* and heat *gently* upon a plaster tablet with the oxidizing flame.

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* *Formed* by grinding together 1 pt. KI, 1 pt. $KHSO_4$, 2 pts. S.

Pb.—Chrome-yellow coat, darker hot, often covers the entire tablet.

Sn.—Brownish-orange coat.

As.—Reddish-orange and yellow coat, darker hot.

Sb.—Orange to peach-red coat, very dark when hot.

Hg.—Gently heated, bright yellow and scarlet coat, very volatile; becomes all scarlet on standing; but if quickly heated, the coat formed is pale yellow and black.

Bi.—Bright scarlet coat surrounded by chocolate-brown with sometimes a reddish fringe.

Tests in Glass Tube.—The glass tube used should be about 3 inches long and $\frac{1}{4}$ inch in diameter, and be of hard glass. One end is closed by fusing it in the Bunsen flame.

Some prefer to use a tube that has had a small bulb blown on one end.

A little of the powdered substance is introduced into the tube so that it rests in the lower or closed end. It is then heated, gently at first, and finally at the highest heat possible.

A. *a.* The substance remains unchanged; ab-

sence of organic matter, volatile or fusible substances, and those containing water of crystallization.

b. The substance blackens; indicates organic matter.

c. The substance fuses without blackening, and no water is given off; add a small piece of charcoal; deflagration indicates nitrates or chlorates.

d. Water is expelled, condensing in upper part of tube; indicates either water of crystallization (such substances generally fuse, and after expulsion of the water solidify again), or that derived from hydroxides or salts yielding water on ignition ($NaHCO_3$), or moisture.

The reaction of the water should be tested; if alkaline it indicates ammonia, if acid a volatile acid (H_2SO_4, HCl, etc.).

B. *Gases are Evolved:*

SO_2, recognized by its odor, indicates either sulphides, sulphites, or sulphates.

NO_2, known by its red color and odor, indicates nitrites or nitrates. Care should be taken not to confuse it with bromine, which also forms a red gas.

Cl, Br, and I may all be liberated, and when alone are easily recognized by their odor and color.

NC or HCN indicates cyanogen compounds decomposable by heat. May be recognized by the odor.

H_2S indicates sulphides (not anhydrous), also thiosulphates. Recognized by odor or lead-acetate paper.

NH_3 indicates ammonium salts or the decomposition of cyanides containing water. Nitrogenous organic matter may also yield ammonia.

C. *A Sublimate Forms:*

S indicates sulphur in the free state or that derived from sulphides, many of which liberate sulphur on heating in this manner. Recognized by forming reddish-brown drops that turn yellow on cooling.

Hg.—Many of the mercury salts volatilize unaltered (the oxygen salts are decomposed on ignition), so that the sublimate in this case may be either metallic mercury or a salt of mercury. If doubtful, make another test by mixing some sodium carbonate with the substance before fusing, and covering this mixture, after placing it in the tube, with a layer of the carbonate, the mercury salts will be decomposed, yielding a sublimate of metallic mercury.

Arsenic.—Metallic arsenic gives its characteristic dark mirror. The oxides yield a white crystalline sublimate of arsenious oxide. The sulphides give sublimates that are reddish yellow while hot and yellow on cooling. The oxide and sulphide are soluble in ammonia.

Antimonious oxide also gives a white crystalline sublimate, insoluble in ammonia.

Besides the tests just given, it is well to heat another portion of the substance mixed with potassium bisulphate (made by heating potassium hydrogen sulphate at a low heat, just sufficient to drive out the water, $2KHSO_4 - H_2O = K_2SO_4, SO_3$) in a glass tube in the same way as in the first test. Many substances not affected by heat alone are decomposed by this reagent. The gases evolved are recognized, as in first test, by their odor color, etc. Fluorine may also be detected in this way, as the gas liberated attacks and corrodes the glass, and should silica be present a drop of water held at mouth of tube will become opaque.

Silica.—Test a few grains of powder in salt of phosphorus bead for silica.

The preliminary examination having been completed, we are ready to proceed with the operation of getting the substance into solution. Should organic matter, such as oil, etc., be present, it must be removed by digesting with proper solvents, as naphtha, etc., or it may in many cases be destroyed by ignition.

Solution.—It is always advisable to follow some systematic plan when dissolving any material given for analysis. The following one, although it may seem tedious at first glance, will be found shorter in the long run than any haphazard attempts at solution.

It will very seldom, if ever, happen that all of the bases and acids provided for will be found in any one mixture, so that the method will be materially shortened in almost all cases. When it is desired to get an idea as to the combinations in which the different constituents of a substance exist, it is necessary to analyze the different solutions separately for both bases and acids. Even this will not always give the true combinations, for interactions may take place on the addition of the solvent that will wholly or partially change them. If it is only required to determine the actual constituents without regard to their combinations, which is usually the case, the different solutions may be analyzed as one mixture, provided they do not precipitate each other. For example, before mixing a water or nitric acid solution with one in hydrochloric acid, the former ought always to be tested with hydrochloric acid to see if any silver, lead, or mercurous salts are present, and if found they should be completely precipitated and filtered off, after which the solutions may be mixed together and analyzed.

The student should make it a rule always to put aside a part of the original material for special tests, and in case of accident to the main analysis.

The solution of a solid substance is conveniently considered under two heads, viz.:

1°. The substance is neither a metal nor an alloy.

2°. The substance is a metal or an alloy.

Substances of the 1° class are to be treated as follows:

A. Boil some of the finely pulverized substance with water, repeating this treatment with fresh portions of water until thoroughly extracted.

a. All dissolves.

Test solution according to Scheme No. V.

b. A residue remains.

Filter, and evaporate to dryness a few drops of e filtrate in a platinum capsule, and see if any appreciable residue remains; if so, test filtrate according to Scheme No. V, or reserve to be combined with acid solution B or C.

B. Residue insoluble in water.

Treat a portion of this residue with dilute hydrochloric acid, applying heat if necessary. If it does not dissolve completely, allow it to settle and then decant the solution, and to the residue add some concentrated hydrochloric acid, and boil.* If everything has now gone into solution the acid liquids are evaporated to small bulk, diluted with water, and precipitated with H_2S in the usual way.

a. In case the foregoing treatment has not effected complete solution, keep the dilute acid liquid, and the one with strong acid containing the undissolved residue for future use.

C. *Hydrochloric acid not having effected complete solution*, take another portion of B and boil with nitric acid, and add water. If all dissolves, evaporate to expel excess of acid, dilute with water, and add to solution A, *b*. Should the addition of water cause a precipitate, it is probably bismuth, which will redissolve on the addition of a few drops of nitric acid. The solution is now tested in the usual way.

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* The presence of carbonate is always revealed at this point by the evolution of CO_2. Sulphides also are frequently detected here by the evolution of H_2S. Also many cyanides.

a. If the boiling nitric acid does not effect complete solution, test a few drops of the liquid, after dilution with water, with dilute hydrochloric acid for silver and lead (mercurous salts would have been oxidized to mercuric).

b. Silver or lead salts are not present.—Mix the nitric acid solution and residue with the hydrochloric acid solutions (B, *a*) and the residue insoluble in that acid; boil the mixture, which now forms aqua regia, for some time; and if there is still a residue left, dilute, and filter and wash precipitate, and treat the latter according to D. The filtrate, after getting rid of the excess of acid by evaporation is combined with the water solution A *b* and analyzed in the usual manner.

c. Silver or lead salts are present.—Dilute the strongly acid solution and filter, washing the residue thoroughly. Then treat this residue first by boiling with fresh hydrochloric acid (not that used in B, *a*), and if this does not dissolve it completely, then add some nitric acid, forming aqua regia, and boil again. If a residue still remains, filter (after dilution) and wash and proceed with it as in D. Reserve filtrate, which is to be mixed with the water and nitric acid solutions later on. Silver and lead salts being present, the water and nitric acid solutions are mixed, the silver, lead, and mercurous salts (the latter from the water solution) precipitated by hydrochloric acid and the filtrate mixed with the aqua regia solution, excess of acid expelled by evaporation to small bulk, the solution diluted and precipitated with H_2S as usual.

D. *Residue insoluble in aqua regia.*

This residue may contain AgCl, $PbSO_4$, $BaSO_4$, $SrSO_4$, $CaSO_4$, SiO_2, and silicates, Al_2O_3, Cr_2O_3, CaF_2, C, S, SnO_2.

a. If the residue insoluble in aqua regia is white, take a few grains of it and add a drop or two of ammonium sulphide; if silver or lead is present it will turn black. In case D is dark colored test a small portion on charcoal or plaster for Ag and Pb. If found, by either test, proceed according to *c*; if not, according to residue 2°.

b. Test another small portion in a glass tube closed at one end for S if its presence has not already been determined in the preliminary tests.

c. Silver and lead salts are present.

Take some of the residue, and heat with a concentrated solution of $NH_4C_2H_3O_2$; filter, and repeat treatment until lead salts are all removed.

FILT. 1°.

Lead salts + 2 parts.

1°.

Add H_2SO_4 – white ppt. = $PbSO_4$.

2°.

Add HCl, filter if necessary, and add a few drops of $BaCl_2$, white ppt. = $BaSO_4$ = H_2SO_4.

RESIDUE 1°.

Warm residue with KCy (if S is present, digest in the cold), filter, and repeat the treatment until Ag salts are all removed.

FILT. 2°.

AgCy, KCy, add $(NH_4)_2S$, brown ppt. = Ag_2S —. Dissolve Ag_2S in hot HNO_3, dilute, filter, and to filtrate add HCl — white ppt. = AgCl = Ag.

RESIDUE 2°.

If S is present, heat residue in porcelain dish until the S has completely volatilized; then mix the residue with $NaKCO_3$ and a little $NaNO_3$, and fuse in a platinum crucible; dissolve the fusion in boiling water, filter and wash.

RESIDUE 3°.

$BaCO_3$, $SrCO_3$, $CaCO_3$ (SiO_2, — Al_2O_3, Cr_2O_3, SnO_2)? Treat with $HC_2H_3O_2$; heat and filter.

FILT. 4°.

$Ba\bar{A}_2$, $Sr\bar{A}_2$, $Ca\bar{A}_2$. Test in the usual way.

RESIDUE 4°.

SiO_2, SnO_2, etc. Place in test-tube with Zn and strong HCl and a few small pieces of platinum—SnO_2, if present, will be reduced to Sn. Dissolve in HCl, and test with $HgCl_2$.

FILTRATE 3°.

Na_2SiO_3, NaF, Na_2CrO_4, $Na_2Al_2O_4$, Na_2SO_4, Na_2SnO_3. (?) Make slightly acid with HCl, and evaporate to dryness; if Cr is present, add a little alcohol; (do not heat much above 100° C.). Add HCl to the dry residue, boil, dilute, and filter.

PPT. 5°.

SiO_2, SnO_2 (?.) Prove SiO_2 by salt of phosphorus bead. Sn by reduction with Zn.

FILTRATE 5°.

NaF, Al_2Cl_6, Cr_2Cl_6, Na_2SO_4, $SnCl_4$ (?). Pass H_2S gas into the solution and filter from any ppt.

FILT. 6.

NaF, Al_2Cl_6, Cr_2Cl_6 + Na_2SO_4.

PPT. 6.

SnS_2, S + Pt + S_2 (?). Add a little concentrated HCl and boil; the tin dissolves as $SnCl_4$. Nearly neutralize and precipitate the tin as metastannic acid with Na_2SO_4.

Add NH_4OH to faintly alkaline reaction and filter.

PPT. 7°.

Al_2. $(OH)_6$, and $Cr_2(OH)_6$). Test in the usual way.

FILTRATE 7°.—(Divide in two parts.)

1.

Acidify with HCl and add $BaCl_2$, white ppt. = $BaSO_4$ = H_2SO_4.

2.

Add $CaCl_2$ and let stand for some time; filter, and test ppt. for Fl by etching test.

A better way to test for Fl would be to take some of residue No. 2 and test that directly, either by etching test, or if silica is present by passing SiF_4 into water.

Metals or Alloys.

Case 2°. The substance is a metal or an alloy. Boil with HNO_3 Sp. Gr. 1. 2, and evaporate nearly to dryness; add a few drops of HNO_3, dilute with water, boil and filter.

<table>
<tr><td colspan="2">Residue 1°.
Residue is white and non-metallic.* Boil with strong solution of $H_2C_4H_4O_6$; if any residue remains filter and wash.</td><td>Filtrate 1°.
Test according to Scheme No. V.</td></tr>
<tr><td>Filtrate 2°.
Add a few drops of HCl, and pass in H_2S, an orange ppt. = Sb_2S_3.</td><td colspan="2">Residue 2°.
Place in a platinum capsule with a piece of zinc and a little strong HCl. The H_2SnO_3 will be reduced to metallic tin. Remove the zinc, dissolve the tin in HCl, and test solution with $HgCl_2$; a white or gray ppt. proves Sn. Gold and platinum, if present, will be left undissolved by the HCl, and should be tested for by dissolving in aqua regia, dividing solution into two parts, and testing for gold with $FeSO_4$, and for platinum with KCl.</td></tr>
</table>

The substance now being in solution, we are ready to proceed with the analysis for the detection of the bases. As the separation of the metals of each group has already been explained. all that is necessary now is to show the connection between the different group schemes. This is done in the following outline, in which it is seen that each group is tested for in the filtrate

---

* If residue is metallic dissolve it in aqua regia and test solution for gold and platinum. Platinum alloyed with a large amount of silver is soluble in nitric acid.

Filt. 1°.

Lead salts + 2 parts.

1°.

Add H_2SO_4 – white ppt. = $PbSO_4$.

2°.

Add HCl, filter if necessary, and add a few drops of $BaCl_2$, white ppt. = $BaSO_4$ = H_2SO_4.

Residue 1°.

Warm residue with KCy (if S is present, digest in the cold), filter, and repeat the treatment until Ag salts are all removed.

Filt. 2°.

AgCy,KCy, add $(NH_4)_2S$, brown ppt. = Ag_2S —. Dissolve Ag_2S in hot HNO_3, dilute, filter, and to filtrate add HCl — white ppt. = AgCl = Ag.

Residue 2°.

If S is present, heat residue in porcelain dish until the S has completely volatilized; then mix the residue with $NaKCO_3$ and a little $NaNO_3$, and fuse in a platinum crucible; dissolve the fusion in boiling water, filter and wash.

Residue 3°.

$BaCO_3$, $SrCO_3$, $CaCO_3$ (SiO_2, — Al_2O_3, Cr_2O_3, SnO_2)? Treat with $HC_2H_3O_2$; heat and filter.

Filt. 4°.

$Ba\bar{A}_2$, $Sr\bar{A}_2$, $Ca\bar{A}_2$. Test in the usual way.

Residue 4°.

SiO_2, SnO_2,* etc. Place in test-tube with Zn and strong HCl and a few small pieces of platinum—SnO_2, if present, will be reduced to Sn. Dissolve in HCl, and test with $HgCl_2$.

Filtrate 3°.

Na_2SiO_3, NaF, Na_2CrO_4, $Na_2Al_2O_4$, Na_2SO_4, Na_2SnO_3. (?) Make slightly acid with HCl, and evaporate to dryness; if Cr is present, add a little alcohol; (do not heat much above 100° C.). Add HCl to the dry residue, boil, dilute, and filter.

Ppt. 5°.

SiO_2, SnO_2 (?.) Prove SiO_2 by salt of phosphorus bead. Sn by reduction with Zn.

Filtrate 5°.

NaF, Al_2Cl_6, Cr_2Cl_6, Na_2SO_4, $SnCl_4$ (?). Pass H_2S gas into the solution and filter from any ppt.

Filt. 6.

NaF, Al_2Cl_6, Cr_2Cl_6 + Na_2SO_4.

Add NH_4OH to faintly alkaline reaction and filter.

Ppt. 6.

SnS_2, S + Pt + S_2 (?). Add a little concentrated HCl and boil; the tin dissolves as $SnCl_4$. Nearly neutralize and precipitate the tin as metastannic acid with Na_2SO_4.

Ppt. 7°.

Al_2, $(OH)_6$, and $Cr_2(OH)_6$). Test in the usual way.

Filtrate 7°.—(Divide in two parts.)

1.

Acidify with HCl and add $BaCl_2$, white ppt. = $BaSO_4$ = H_2SO_4.

2.

Add $CaCl_2$ and let stand for some time; filter, and test ppt. for Fl by etching test.

A better way to test for Fl woul be to take some of residue No. 2 and test that directly, either by etchin test, or if silica is present by passing SiF_4 into water.

into solution, that the mercurous salt may have been changed to mercuric. In cases of this kind, if mercuric salts only have been found in the regular course of analysis, it is always necessary to test specially for mercurous compounds. This may be done by digesting some of residue B with cold dilute hydrochloric acid and filtering; the residue is then washed with boiling water and tested with ammonia in the usual way for mercurous salt.

If tin has been found, the oxide present is determined by testing some of the hydrochloric acid solution (water solution also should be tested in same way) with mercuric chloride for stannous salts and with sodium sulphate or nitrate for stannic.

The two oxides of iron are tested for in the hydrochloric acid and water solutions with potassium ferricyanide for ferrous and thiocyanate for ferric salts.

For arsenic, the difference in color of the silver salts, the tests with copper sulphate, the magnesium mixture test, and the time required for precipitation by H_2S will generally show which oxide is present.

FILT. 1°.

Lead salts + 2 parts.

1°.

Add H_2SO_4 – white ppt. = $PbSO_4$.

2°.

Add HCl, filter if necessary, and add a few drops of $BaCl_2$, white ppt. = $BaSO_4$ = H_2SO_4.

RESIDUE 1°.

Warm residue with KCy (if S is present, digest in the cold), filter, and repeat the treatment until Ag salts are all removed.

FILT. 2°.

AgCy,KCy, add $(NH_4)_2S$, brown ppt. = Ag_2S —. Dissolve Ag_2S in hot HNO_3, dilute, filter, and to filtrate add HCl — white ppt. = AgCl = Ag.

RESIDUE 2°.

If S is present, heat residue in porcelain dish until the S has completely volatilized; then mix the residue with $NaKCO_3$ and a little $NaNO_3$, and fuse in a platinum crucible; dissolve the fusion in boiling water, filter and wash.

RESIDUE 3°.

$BaCO_3$, $SrCO_3$, $CaCO_3$ (SiO_2, — Al_2O_3, Cr_2O_3, SnO_2)? Treat with $HC_2H_3O_2$; heat and filter.

FILT. 4°.

$Ba\bar{A}_2$, $Sr\bar{A}_2$, $Ca\bar{A}_2$. Test in the usual way.

RESIDUE 4°.

SiO_2, SnO_2, etc. Place in test-tube with Zn and strong HCl and a few small pieces of platinum—SnO_2, if present, will be reduced to Sn. Dissolve in HCl, and test with $HgCl_2$.

FILTRATE 3°.

Na_2SiO_3, NaF, Na_2CrO_4, $Na_2Al_2O_4$, Na_2SO_4, Na_2SnO_3. (?) Make slightly acid with HCl, and evaporate to dryness; if Cr is present, add a little alcohol; (do not heat much above 100° C.). Add HCl to the dry residue, boil, dilute, and filter.

PPT. 5°.

SiO_2, SnO_2 (?.) Prove SiO_2 by salt of phosphorus bead. Sn by reduction with Zn.

FILTRATE 5°.

NaF, Al_2Cl_6, Cr_2Cl_6, Na_2SO_4, $SnCl_4$ (?). Pass H_2S gas into the solution and filter from any ppt.

FILT. 6.

NaF, Al_2Cl_6, Cr_2Cl_6 + Na_2SO_4.

Add NH_4OH to faintly alkaline reaction and filter.

PPT. 6.

SnS_2, S + Pt + S_2 (?). Add a little concentrated HCl and boil; the tin dissolves as $SnCl_4$. Nearly neutralize and precipitate the tin as metastannic acid with Na_2SO_4.

PPT. 7°.

$Al_2(OH)_6$, and $Cr_2(OH)_6$). Test in the usual way.

FILTRATE 7°.—(Divide in two parts.)

1.

Acidify with HCl and add $BaCl_2$, white ppt. = $BaSO_4$ = H_2SO_4.

2.

Add $CaCl_2$ and let stand for some time; filter, and test ppt. for Fl by etching test.

A better way to test for Fl would be to take some of residue No. 2 and test that directly, either by etching test, or if silica is present by passing SiF_4 into water.

a part may be fused with barium hydrate, as explained under tests for silicic acid.

Cyanides and Ferro- and Ferricyanides insoluble in acids are best decomposed by boiling with strong sodium or potassium hydrate, then adding sodium carbonate and boiling again. On filtering the residue will be free from cyanogen (except silver cyanide), and the filtrate will contain all of the cyanogen in combination with the alkalies, and besides this all of those metals whose hydroxides are soluble in alkali (Zn, Al, Pb, As, etc.). Before testing this solution for cyanide, ferro- and ferricyanide, etc., sodium sulphide should be added to it drop by drop as long as it causes any precipitate, but avoid a large excess of the reagent. This treatment removes those metals whose sulphides are insoluble in alkalies (Zn, Pb). Filter and add dilute sulphuric acid to the filtrate until it is slightly acid, then add H_2S if the solution does not already smell of that gas. This will precipitate any metals of the sixth group, and after filtering the solution may be tested for the cyanogen acids, as already explained.

REAGENTS.

Hydrochloric acid, HCl (strong), sp. gr. 1.12, 24% acid.

Hydrochloric acid HCl (dilute), sp. gr. 1.06.

Nitric acid, HNO_3 (strong), sp. gr. 1.2, 32% acid.

Nitric acid, HNO_3 (dilute), sp. gr. 1.1.

Sulphuric acid, H_2SO_4 (conc.), sp. gr. 1.84, 95% acid.

Sulphuric acid, H_2SO_4 (dilute), sp. gr. 1.14.

Acetic acid, $HC_2H_3O_2$, sp. gr. 1.04, 30% acid.

Hydrosulphuric acid, H_2S, is used either in the gaseous form or as a solution in water. It is generally prepared from ferrous sulphide (FeS) and hydrochloric or sulphuric acid. The water solution is obtained by saturating water with the gas. It does not keep well and must be freshly prepared from time to time.

Tartaric acid, $H_2C_4H_4O_6$ (crystallized), dissolved in water as needed for use, 1 part acid to 3 of water.

Potassium hydroxide, KOH, solution of sp. gr. 1.125, 15% KOH.

Sodium hydroxide may be used instead of the above.

Potassium chromate, K_2CrO_4, 1 part to 10 parts water.

Ammonium hydroxide, NH_4OH, solution of sp. gr. 0.96 = 10% NH_2.

Sodium carbonate, $Na_2CO_3,10H_2O$, 2.7 parts to 5 of water.

Sodium hydrogen phosphate, $Na_2HPO_4,12H_2O$, 1 part to 10 parts of water.

Sodium acetate, $NaC_2H_3O_2,3H_2O$, 1 part to 10 parts of water.

Sodium hypochlorite, NaClO. Some bleaching powder (chloride of lime) is dissolved in water, and sodium carbonate solution added as long as a precipitate forms. Allow the precipitate to settle and then siphon off the clear liquid for use.

Ammonium carbonate, $(NH_4)_2CO_3$, 1 part of salt, 4 parts of water, and 1 part of ammonium hydroxide.

Ammonium sulphide, $(NH_4)_2S$ and $(NH_4)_2S_x$. Two solutions of ammonium sulphide are required, one of the normal sulphide for the precipitation of the 3° and 4° groups and one of polysulphide for the separation of 5° and 6° groups.

The method ordinarily used for the preparation of the normal sulphide does not yield this compound according to the researches of Bloxam (see *Jour. Chem. Soc.*, Apr. 1895), and he gives the following: H_2S gas is passed into ammonium hydroxide solution and small portions are taken from time to time and tested as follows:

An *excess* of solution of recrystallized cupric sulphate (1 cc. = about 0.1 grm. of $CuSO_4$) is placed in a flask, water is added, and then a few drops of the sulphide solution, and the mixture well shaken. It is then filtered (the filtrate must have a blue color, showing the presence of an excess of copper sulphate) and the precipitate washed with boiling water until *all the copper sulphate has been washed out.* Dilute solution of potassium hydroxide is added to the filtrate a drop at a time. If the first drop or two produces a precipitate, showing that the solution is neutral, the precipitate of sulphide, that has been thoroughly washed, is shaken with ammonium hydroxide and filtered. A blue filtrate shows that the portion of ammonium sulphide tested contained free ammonia, and more H_2S is required. If no blue color is produced, the solution then consists of $(NH_4)_2S$. If on testing the first filtrate with KOH it had shown an acid reaction, this would indicate the presence of NH_4HS. The following equations explain the reaction taking place under the different conditions:

$$\begin{aligned}(a)\ & 3CuSO_4 + 2NH_4HS \\ & = \underbrace{2CuS} + (NH_4)_2SO_4 + H_2SO_4 + CuSO_4.\end{aligned}$$

$$\begin{aligned}(b)\ & 2CuSO_4 + (NH_4)_2S \\ & = \underbrace{CuS} + (NH_4)_2SO_4 + CuSO_4.\end{aligned}$$

$$\begin{aligned}(c)\ & 3CuSO_4 + (NH_4)_2S + 2NH_4OH \\ & = \underbrace{CuS + Cu(OH)_2} + 2(NH_4)_2SO_4 + CuSO_4.\end{aligned}$$

From the above equations it is evident that when the filtrate has an acid reaction, as in (*a*), the solution of sulphide contains NH_4HS. If the reaction is neutral and the precipitate gives no blue solution on treatment with ammonia, then the solution must be one of $(NH_4)_2S$ (*b*). It is better that the solution contain some NH_4HS rather than free ammonia.

The polysulphide is made from the normal one by addition of a little free sulphur, which soon dissolves and the solution becomes of a red color.

Ammonium oxalate $(NH_4)_2C_2O_4$, 1 part to 24 parts of water.

Ammonium chloride, NH_4Cl, 1 part to 8 parts of water.

Ammonium sulphate, $(NH_4)_2SO_4$, 1 part to 5 parts of water.

Ammonium molybdate, $(NH_4)_6Mo_7O_{24}$. Dissolve 1 part of molybdic acid MoO_2 in 4 parts of ammonium hydroxide solution, filter quickly, and pour *into* 15 parts by weight of nitric acid, sp. gr. 1.2.

Ammonium acetate, $NH_4C_2H_3O_2$. Add acetic acid to ammonium hydroxide until solution is neutral.

Ammonium thiocyanate, NH_4CNS, 1 part to 10 parts of water.

Potassium ferrocyanide, $K_4(FeC_6N_6)$, 1 part to 10 parts of water.

Barium chloride, $BaCl_2,2H_2O$, 1 part to 10 parts of water.

Calcium hydroxide (lime-water), $Ca(OH)_2$, a saturated solution.

Calcium chloride, $CaCl_2,6H_2O$, 1 part to 5 parts of water.

Calcium sulphate, $CaSO_4$,saturated solution.

Magnesium sulphate, $MgSO_4,7H_2O$, 1 part to 10 of water.

Ferric chloride, Fe_2Cl_6, 1 part to 10 parts of water.

Lead acetate, $Pb(C_2H_3O_2)_2$, 1 part to 10 parts of water.

Silver nitrate, $AgNO_3$, 1 part to 20 parts of water.

Mercuric chloride, $HgCl_2$, 1 part to 16 parts of water.

Stannous chloride, $SnCl_2$, 1 part to 10 parts of water.

Some metallic tin and a little free hydrochloric acid should be kept in this solution to prevent oxidation of the stannous chloride.

Hydrochloroplatinic acid, H_2PtCl_6, 1 part to 10 parts of water.

Cobaltous nitrate, $Co(NO_3)_2$, 1 part to 10 parts of water.

Potassium pyroantimoniate, $K_2H_2Sb_2O_7$, dissolved as required in hot water and the solution filtered.

Potassium ferricyanide, $K_6(FeC_6N_6)_2$. It is best to keep this reagent in the dry state and dissolve in water when needed, as its solution when kept is liable to partial reduction to ferrocyanide.

Potassium cyanide, KCN, dissolved in water as required.

Barium carbonate, $BaCO_3$. Prepared by precipitating a solution of barium chloride with ammonium carbonate, washing the precipitate thoroughly, and then placing it in a bottle and covering with water. When wanted for use it is shaken up with the water and the milky-looking solution used.

Ferrous sulphate, $FeSO_4,7H_2O$, dissolved in cold water as required.

Sodium potassium carbonate. Used in preference to either carbonate alone, as it is more easily fusible. Made by thoroughly mixing 13 parts of anhydrous potassium carbonate with 10 of dry sodium carbonate.

Borax, $Na_2B_4O_7,10H_2O$.

Sodium ammonium hydrogen phosphate (phosphorus salt; microcosmic salt), $NaNH_4HPO_4,4H_2O$.

When fused it becomes sodium metaphosphate, $NaPO_3$.

Potassium chlorate, $KClO_3$.

Lead dioxide, PbO_2.

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